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REMOVAL OF HEAVY METALS FROM MINE DRAINAGE BY PRECIPITATION

Laurence W. Ross

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REMOVAL OF HEAVY METALS FROM MINE DRAINAGE BY PRECIPITATION

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Grant No. 14040 FZC
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ABSTRACT

Heavy metals in mine drainage waters of the Rocky Mountains can be removed by a two-stage process consisting of (1) neutralization followed by (2) sulfide treatment. The first stage removes ferric and aluminum hydroxides, and the second (sulfide) stage precipitates the heavy metals that are most objectionable as pollutants, and that are of possible interest for economic recovery. The two-stage process has been demonstrated in the laboratory and in a field experiment.

In the field, powdered lime was employed for neutralization, and barium sulfide was employed as sulfide source in a two-stage treatment tank. The ferric and aluminum hydroxides failed to settle when even the slightest winds disturbed the surface of the settling pond, but the sulfides settled within a few feet downstream. The measured pH of treated streams has proven entirely satisfactory for control of chemical additions.

A computer program based on published values of equilibrium constants and solubility-product constants is capable of adequate prediction of the required chemical quantities for treatment, and of the resulting metal concentrations in solution.

The economics of chemical addition indicates that recovery of sulfides (CuS, ZnS) for sale to smelters can partially offset the cost of treatment, but never completely.

This report was submitted in fulfillment of Grant Number 14040 FZC between the Environmental Protection Agency (EPA) and the grantee, University of Denver, Denver, Colorado 80210.

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SECTION I

CONCLUSIONS

Mine drainage waters of the Rocky Mountains often contain considerable quantities of heavy metals, which connot be removed by neutralization alone. A two-stage process of (1) neutralization, followed by (2) addition of sulfide chemicals is shown to be effective in removing practically all polluting metals at pH 6.5. This result has been demonstrated in the laboratory and verified in the field.

A field treatment installation is feasible with very simple facilities. The operations of chemical addition and sedimentation of the resulting precipitates can be achieved in facilities essentially of earthwork, with a minimum of construction and no process vessels required. Auxiliary transfer and storage facilities consist of lime solids-handling equipment; sulfide solution storage, pumping, and metering equipment; and control instrumentation. These are relatively inexpensive, but the necessity of storing solid lime and of handling and mixing sulfide (BaS) is a critical economic factor.

Barium sulfide (BaS) is recommended for sulfide treatment because Ba does not persist in the treated water, being completely precipitated as $BaSO_4$. Lime (CaO) is selected for neutralization on economic grounds.

A large settling pond is not necessary for recovery of the sulfide precipitates (CuS, ZnS) of economic interest, because these minerals precipitate very rapidly. However, the hydroxides (e.g., $Fe(OH)_3$, $Al(OH)_3$) from the neutralization stage do not readily precipitate, and this requires consideration of a second settling pond or of filtration through earth.

There is evidence that addition of cationic flocculant in ppm

concentrations aids in the sedimentation of sulfides to a significant extent.

Computer simulation of the response of mine drainage water to chemical addition is feasible by use of published solubility-product constants and equilibrium constants.

SECTION II

RECOMMENDATIONS

The two-stage treatment process described in this report seems fully capable of treatment of any metal-bearing mine drainage stream. A continuous field test, on a drainage stream from an active or inactive mine, is desirable in order to confirm the ease of controlling metal removal, with pH as the criterion.

The fractionation of hydroxides ($Fe(OH)_3$, $Al(OH)_3$) from sulfides (CuS, ZnS, MnS, etc.) needs to be explored further, in order to test the feasibility of achieving relatively pure sulfide precipitates under field conditions. It appears that a perfectly quiescent settling pond may achieve hydroxide precipitation, so that sulfides can be precipitated in a second pond without hydroxide contamination.

Finally, it is recommended that less expensive sources of sulfide than those commercially available (e.g., BaS, Na_2S, NaHS) be investigated. This points directly to biological production of H_2S *in situ* from the plentiful SO_4^{2-} available in drainage waters. The possibility of biological generation of S^{2-} has been demonstrated by several investigators (including the present investigators), and merits further study.

SECTION III

INTRODUCTION

THE PROBLEM OF METAL-BEARING MINE DRAINAGE WATERS OF THE ROCKY MOUNTAINS

The Rocky Mountains have been the scene of intense mining activity for more than a century. In several districts, the mineral formations are highly pyritic, and the drainage from inactive as well as active mines is intensely acidic and loaded with metals toxic to aquatic life.

The Red Mountain district of the San Juan Mountains in southwestern Colorado, where the field treatment portion of the present study was performed, is characterized by a series of tertiary volcanic rocks, intruded by a later volcanic pipe. Sulfide minerals are especially prevalent in the pipe. The result is a geologic situation that is especially conducive to metal-bearing acid mine drainage, without the buffering influence of alkaline minerals that are common elsewhere in the mining regions of the Rocky Mountains. Such a predominance of sulfide minerals is not the usual situation in the Rocky Mountains, but there are several primary sulfide mineral districts in Colorado, Idaho, Montana and Utah.

The characteristic feature of the metal-bearing drainage, as illustrated in Table I, is high toxicity combined with relatively small volume. Figures 1 and 2 show the two typical inactive mines that supplied water for this study (Mines J and K). Interestingly, no gold is found in the drainage of the region, and very little

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TABLE I

RESULTS OF ANALYSES - METALS (HEAVY AND/OR TOXIC)

Water from Mine K

Date Sample Coll'td.	Field pH	Arsenic As µg/l	Cadmium Cd µg/l	Copper Cu µg/l	Iron Total Fe µg/l	Lead Pb µg/l	Manganese Mn µg/l	Nickel Ni µg/l	Aluminum Al µg/l	Zinc Zn µg/l	$SO_4^=$ mg/l
8/28/68	-	11,300	613	71,600	422,000	410	9,110	300	32,200	181,000	1,980
9/12/68	2.8	14,300	744	87,000	525,000	450	12,700	350	39,300	215,000	2,480
10/01/68	2.6	16,500	814	99,200	609,000	390	14,700	420	46,200	239,000	2,840
10/24/68	3.0	18,200	814	101,000	651,000	390	15,100	480	48,200	242,000	3,040
11/08/68	-	20,600	910	115,000	714,000	360	16,800	480	54,300	264,000	3,380
12/03/68	-	22,000	1,000	128,000	800,000	440	19,000	510	62,500	294,000	3,820
4/28/69	2.7	12,300	460	61,900	406,000	460	9,510	240	31,600	135,000	1,830
6/04/69	2.8	10,700	660	74,900	423,000	500	7,000	250	29,000	174,000	1,930
6/17/69	3.1	7,750	520	60,100	336,000	40	5,040	230	24,600	246,000	1,570
7/02/69	2.6	6,010	440	51,600	291,000	400	4,520	190	20,800	122,000	1,400

Data: Federal Water Pollution Control Administration

FIGURE 1. Mine J, in the Red Mountain District of Southwestern Colorado. It was Built Principally as a Drainage Tunnel for Other Mines Nearby.

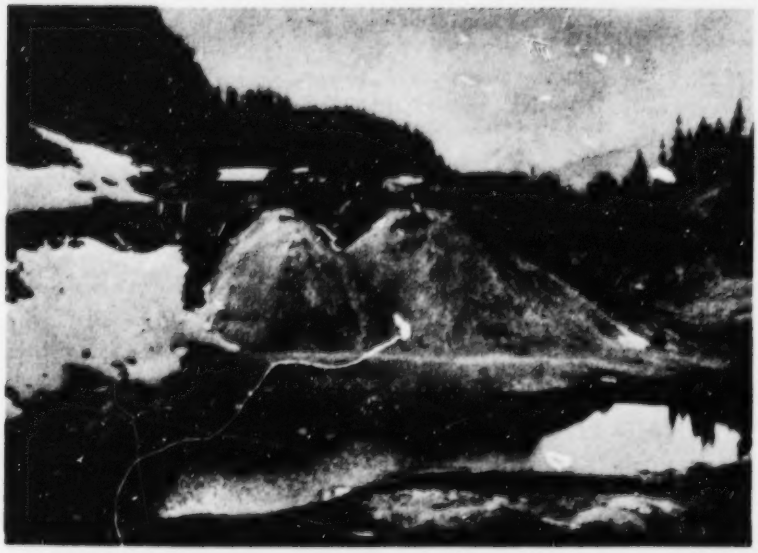

FIGURE 2. Mine K, near Red Mountain Pass. Drainage Enters the Pond at the Left of the Trailings Piles.

silver or lead, although all three metals are extensively mined there. This fact is influential when metal recovery is discussed as a means of offsetting the cost of pollution abatement.

SECTION IV

TECHNICAL PARAMETERS OF METAL-BEARING MINE DRAINAGE

Drainage waters from mines in the sulfide-mineral districts of the Rocky Mountains are often highly acidic. The present investigators, for example, have found pH 1.4 in the drainage pond of mine K (Fig. 2), and the typical value for raw drainage water is about 2.5 to 3.0 everywhere in such regions. The oxidation-reduction potential of these mine drainage waters is generally about +450 mV.

Dissolved metals in these drainages include Fe, Zn, Al, Cu, Mn, roughly in that order of concentration, and may also include quantities of As and Hg at levels that are considered toxic. Iron is practically always measured as total Fe (see Table I) because of the difficulty of discriminating Fe^{+3} and Fe^{+2}, especially under field conditions.

All these metals are capable of removal either by precipitation as insoluble species (oxide, hydroxide, etc.) or by adsorption on various minerals in one or another of their dissolved states. There are several modern studies of hydroxide precipitation available (1,2,3,4) and one in which sulfide precipitation is considered (5). Adsorption has been studied very recently, and work is continuing. Perhaps the principal natural mechanism of elimination of toxic metals (or "heavy" metals) from mine drainage waters is dilution by ambient run-off from springs, rainfall, and snowmelt, which will raise the pH sufficiently to cause precipitation of the metal as hydroxide. Despite these natural mechanisms, hundreds of miles of streams in the Rocky Mountains are severely polluted and incapable of supporting aquatic life.

The present investigation concerns the deliberate precipitation of metals by chemical addition, involving the following general process:

$$mM^{+d} + dD^{-m} \xrightarrow{x_i} M_mD_d\downarrow \qquad (1)$$

where M denotes metallic cation of valence (+d)

D denotes anion of valence (-m)

x_i is the conversion, in moles, to insoluble species M_mD_d.

For example, the most common precipitation process associated with mine drainage waters is

$$Fe^{+3} + 3\ OH^- \longrightarrow Fe(OH)_3$$

in which d = 3, m = 1, M is ferric ion Fe^{+3}, and D is hydroxyl ion OH^-.

For precipitation reactions of this type, the "solubility product" is defined as

$$[M]^m\ [D]^d = K_{sp_i}$$

in which the activity of the solid M_mD_d phase is assumed unity, i.e., $a_{solid} = 1$. With this terminology, a mass blance for the situation where precipitating chemicals are added yields (with brackets denoting molar concentrations as usual):

$$\left[\frac{M_j^{+d} - m_j x_i}{V}\right]^m \left[\frac{D_k^{-m} - \sum d_k x_i}{V}\right]^d = K_{sp_i} \qquad (2)$$

where V is solution volume, i denotes solid phase, j denotes cation, and k denotes anion.

In aqueous medium, the dissociation of water must be considered:

$$H^+ + OH^- \xrightarrow{y_1} HOH. \qquad (3)$$

When the anion is sulfide ion, S^{-2}, two additional equilibria must be considered:

$$H^+ + S^{-2} \xrightarrow{y_2} HS^- \qquad (4)$$

$$H^+ + HS^- \xrightarrow{y_3} H_2S. \qquad (5)$$

These three equilibria may also be expressed in terms of their respective equilibrium constants, by means of a mass balance, as follows:

$$\left[\frac{H^+ - y_1 - y_2 - y_3}{V}\right]\left[\frac{OH^- - y_1 - \Sigma d_j x_i}{V}\right] = K_{e_{H_2O}} \qquad (6)$$

$$\frac{\left[\frac{H^+ - y_1 - y_2 - y_3}{V}\right]\left[\frac{S^{-2} - y_2 - \Sigma d_j x_i}{V}\right]}{\left[\frac{HS^- + y_2 - y_3}{V}\right]} = K_{e_{HS^-}} \qquad (7)$$

$$\frac{\left[\frac{H^+ - y_1 - y_2 - y_3}{V}\right]\left[\frac{HS^- + y_2 - y_3}{V}\right]}{\left[\frac{H_2S + y_3}{V}\right]} = K_{e_{H_2S}}. \qquad (8)$$

Here $\Sigma d_j x_i$ represents the demand of metal precipitation reactions

upon the anionic species OH^- and S^{-2}, and $\Sigma d_j y_i$ represents the demand upon these anions by reactions (3), (4) and (5). It should be noted that the molar concentration $[OH^-]$ may be expressed as $[10^{14-pH}]$, which is the procedure actually used in computation, as described in Section VII below.

The values of K_{sp} and K_e for the species involved in the present investigation are subject to wide discrepancies, in the published literature. It is not unusual to observe a variation of two or three orders of magnitude, depending on the source. This point will be discussed in relation to the findings of the investigation, in Section VII below, where "best values" of K_{sp} and K_e for the systems of interest will be recommended.

Only the simplest precipitation mechanisms are considered in the present investigation. A vast number of ionic reactions are possible with the species of interest in aqueous medium, and these are catalogued in references 7 and 8. The justification for considering only the simplest is that these are the most favorable equilibrium constants under the given conditions, and the other possible reactions occur to negligible extent.

SECTION V

PRELIMINARY EXPERIMENTAL TESTS

1. Simulated Drainage Waters

From examination of solubility product constants, it seemed apparent that hydroxides and sulfides were the only reasonable chemical species by which heavy metals could be precipitated from mine drainage waters. Experimental tests of precipitation were undertaken in the laboratory.

Initial experiments were conducted with pure solutions, prepared in the laboratory. Figures 3 and 4 show that solutions containing Fe, Zn and Cu respond to sulfide addition in a fashion very close to theoretical expectations. This suggests that metals could be fractionated from solution, which is economically attractive, as discussed below.

These three metals, when alone in solution, respond to sulfide addition in essentially theoretical fashion. However, manganese departs significantly from stoichiometric agreement with total sulfide added (Fig. 5). This behavior indicates that Mn precipitation must be considered in combination with the reactions between sulfide ion and water, eqns. (4) and (5) in the preceding section.

Hydroxide precipitation is not investigated in experiments of this type, because it is regarded strictly as a means of Fe and Al elimination and pH adjustment.

The response of dissolved Fe, Cu Zn and Mn to addition of BaS and $Na_2S \cdot 9H_2O$ solutions is practically identical. This indicates that the sulfides are completely dissociated in solution. Barium sulfide, BaS, is regarded as the leading contender for field use because Ba precipitates as $BaSO_4$, while Na remains in solution,

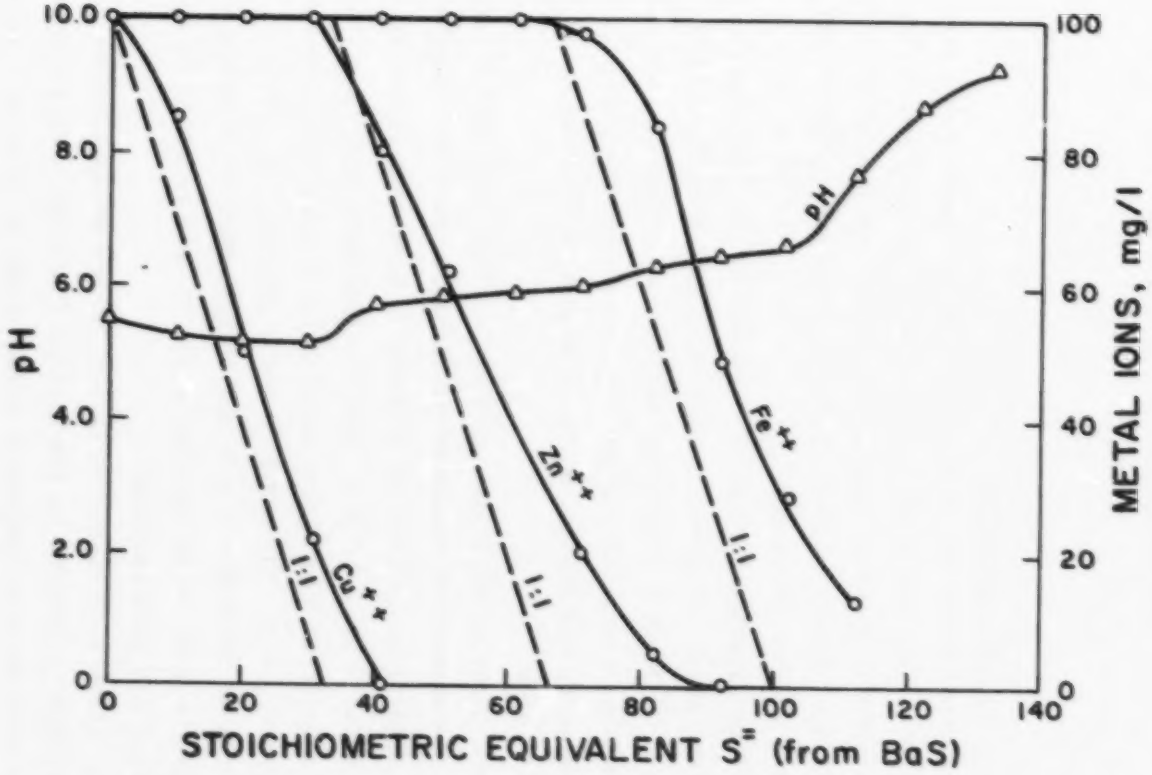

Fig. 3. Fractionation of Dissolved Cu^{++}, Zn^{++} and Fe^{++} From Solution by BaS. The Solution Contained 100 mg/l of Each Metal. Dashed Lines are Stoichiometric Lines.

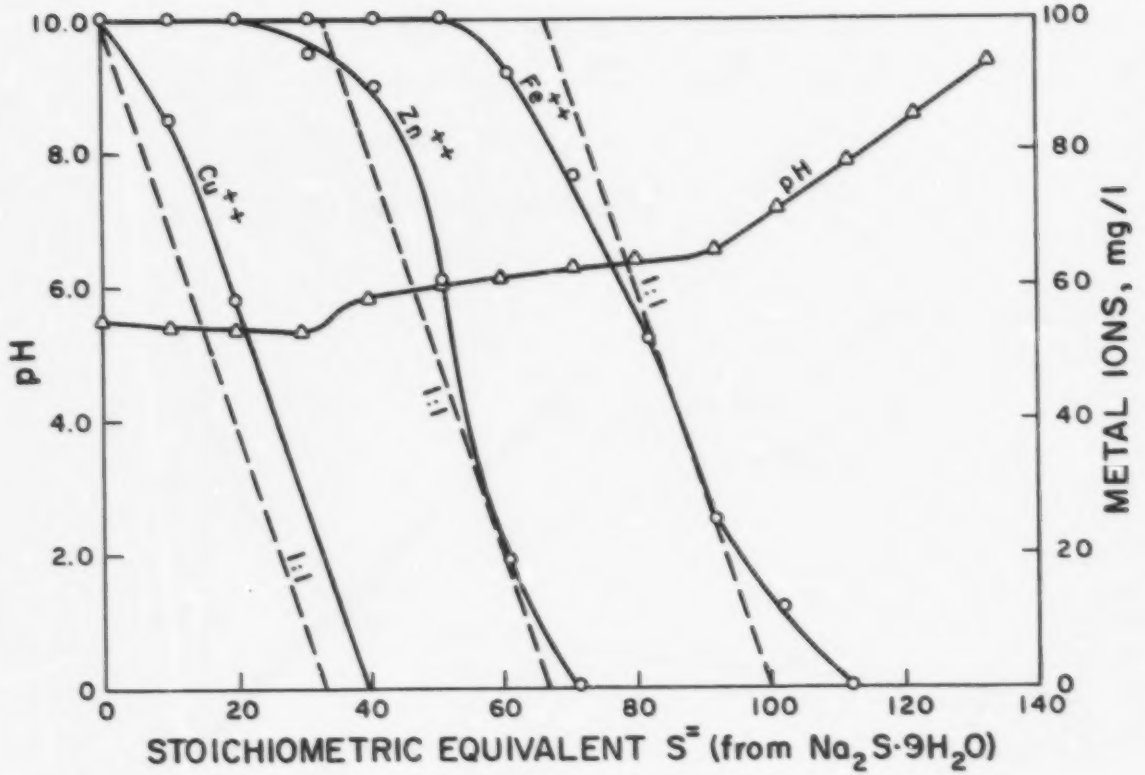

Fig. 4. Fractionation of Cu^{++} and Fe^{++} From Solution by $Na_2S \cdot 9H_2O$. The Solution Contained 100 mg/l of Each Metal. Dashed Lines are Stoichiometric Lines.

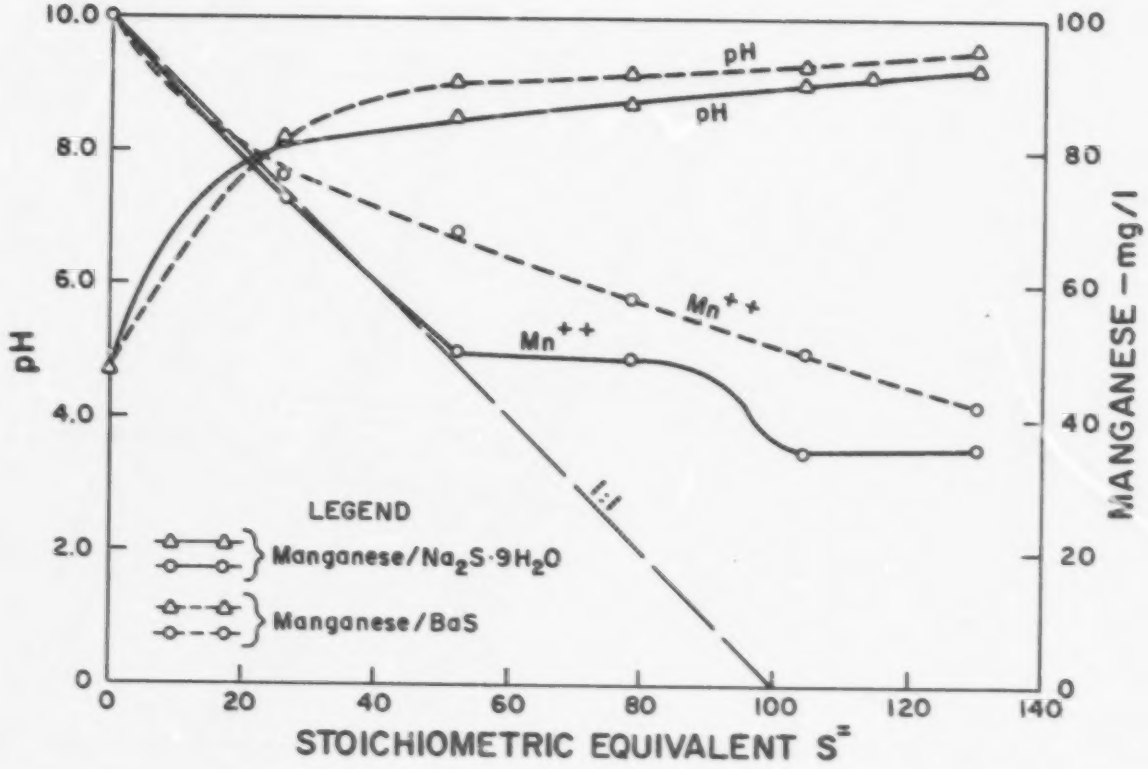

Fig. 5. Response of Dissolved Mn^{++} (100 mg/l) to Addition of 0.02 M Sulfide Solutions.

in violation of the announced policy of the EPA regarding addition of polluting species to waterways. In addition, BaS is less expensive than $Na_2S \cdot 9H_2O$, although more expensive than NaHS in commercial quantities.

2. Actual Drainage Waters

When actual drainage waters are examined, the situation is much more difficult to analyze. The most useful tool (and certainly the simplest) seems to be characteristic titration curves, also called "fingerprint curves" that show the pH response of water samples to addition of sulfide or hydroxide.

Figure 6 shows characteristic curves for mines J and K, from titrations made on drainage waters collected in June, 1970. These curves permit estimates of the metal content as follows:

Mine J	34.4 meq/l
Mine K	11.2 meq/l

Measurements of metals on the same samples yielded the following concentrations:

	Mine J	Mine K
Fe (total), mg/l	860	310
Zn, mg/l	280	141
Cu, mg/l	10.5	2.0

At this time, the investigation did not have access to efficient means of analyzing metal concentrations. The concentrations above were measured by the Department of Health, State of Colorado.

The characteristic curves shown in Figs. 7, 8 and 9 represent drainage waters in Idaho and Montana, from samples taken in June, 1971. The drainage labeled BTP (Fig. 9) is by far the most potent discovered in the entire investigation. It was taken from an open

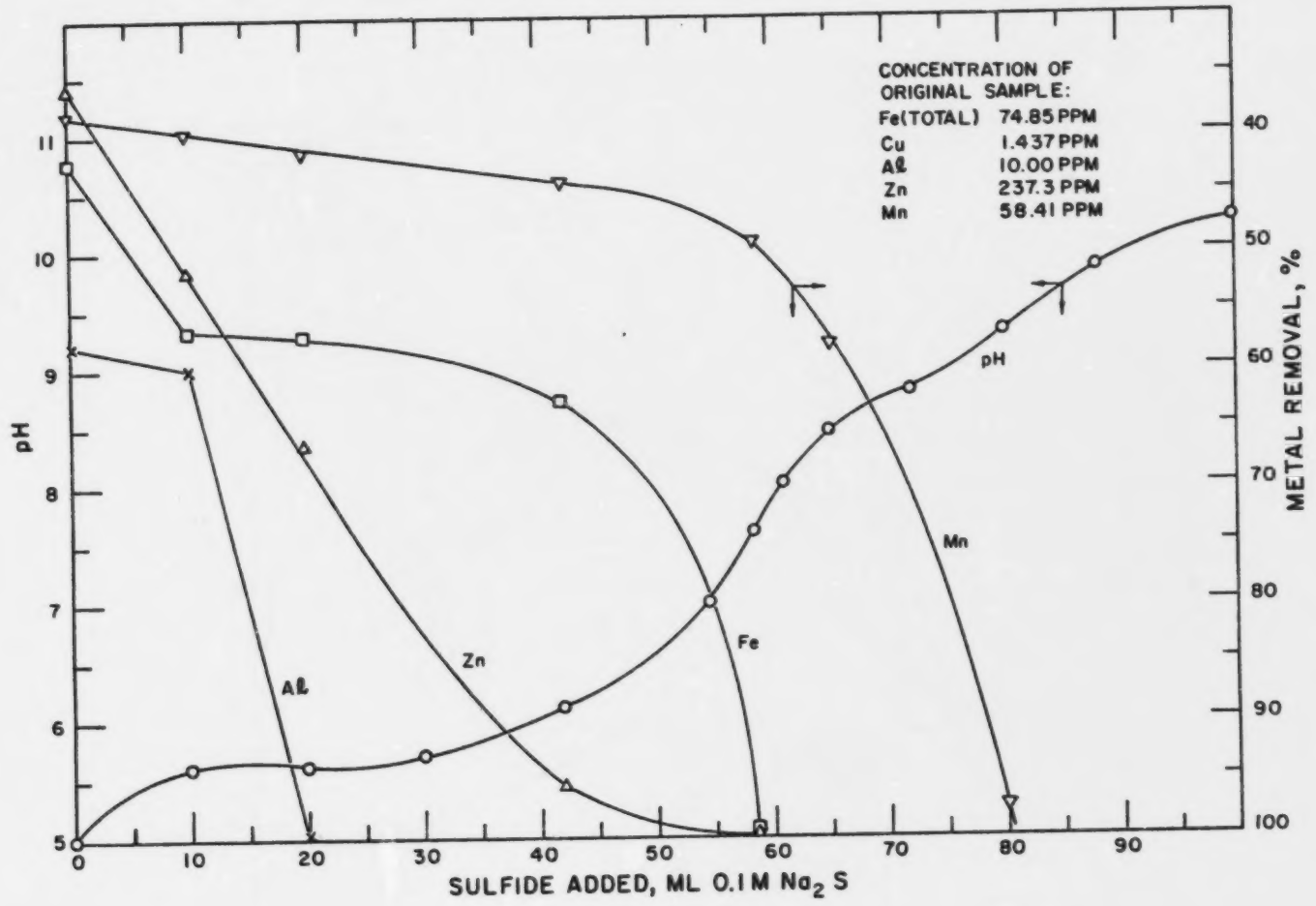

Fig. 7. Treatment Curves for Drainage Water of Min BH (Idaho). Treatment with Sulfide Begins After Neutralization to pH 5.

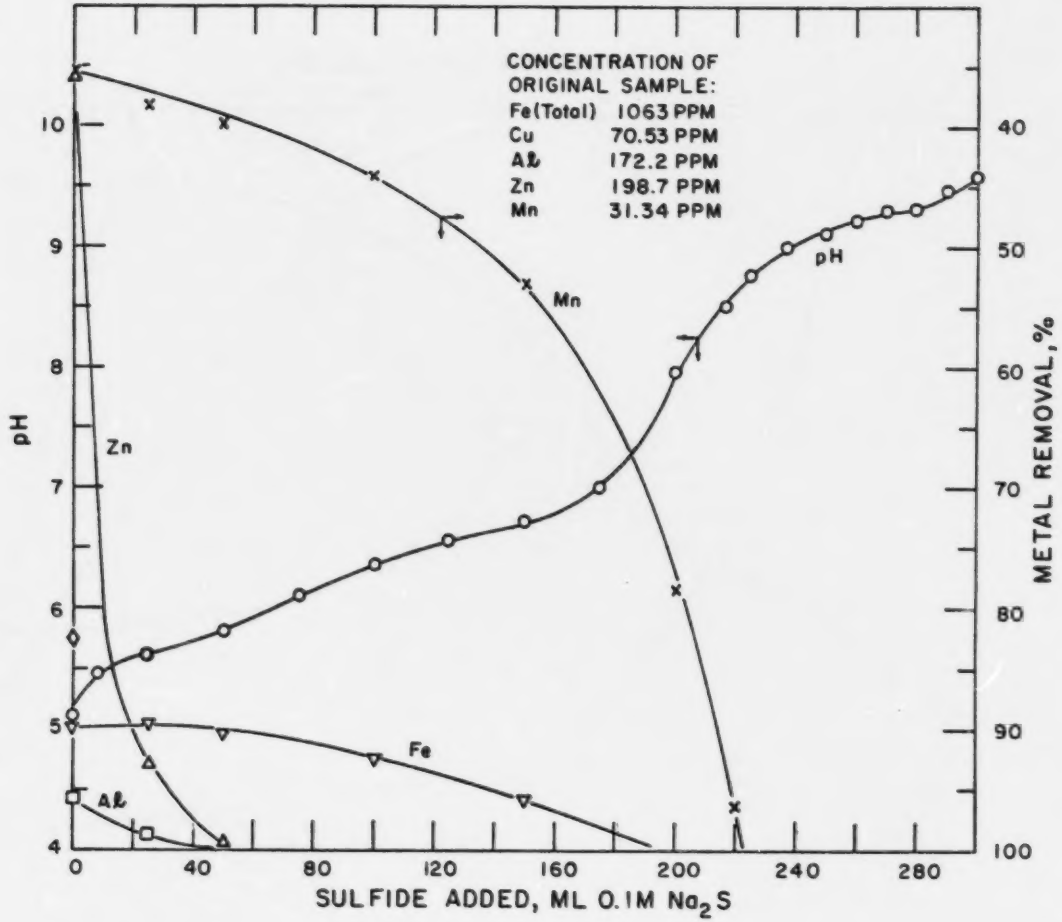

Fig. 8. Treatment Curves for Creek Water, Source BB (Montana). Treatment with Sulfide Begins After Neutralization to pH 5.

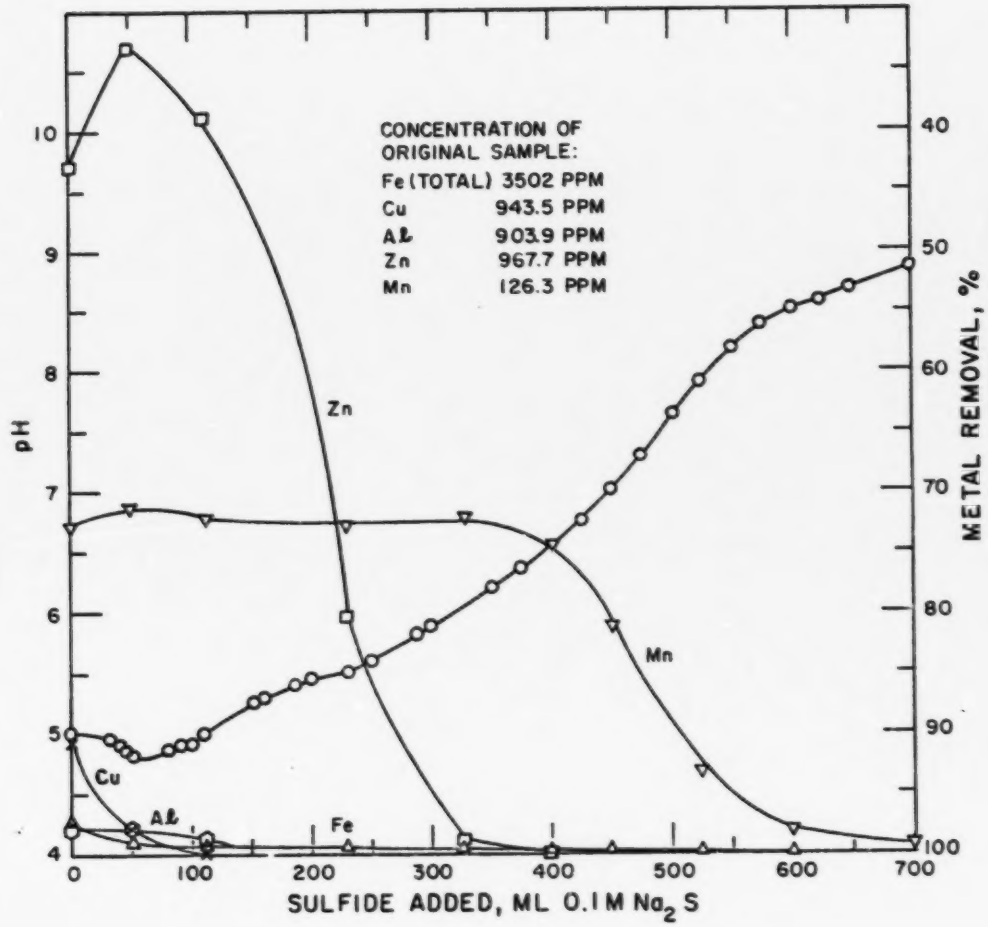

Fig. 9. Treatment Curves for Ditch Water, Source BT (Montana). Treatment with Sulfide Begins After Neutralization to pH 5. This water Had the Highest Metals Concentration of any Waters Found in the Rocky Mountains.

culvert in a Montana city, and it was probably drainage from a mining or milling operation nearby.

A final set of characteristic curves is shown in Fig. 10 representing several relatively benign drainages from Colorado, Idaho, and Montana. Several are definitely alkaline, even though taken from mining regions where sulfide deposits are typical.

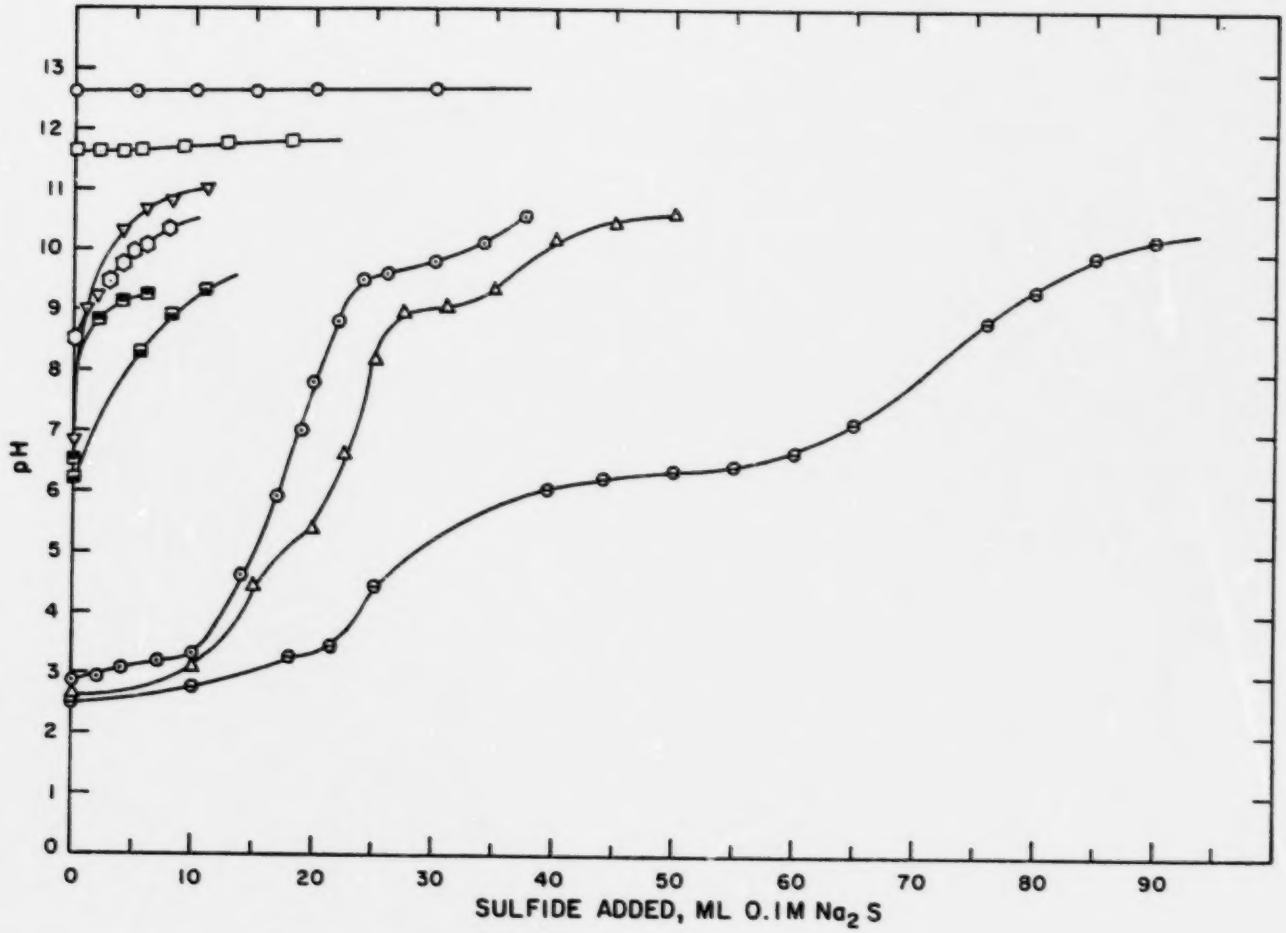

Fig. 10. Response Curves of Several Drainage Waters, Sampled from Open Sources in Colorado, Idano and Montana. Some are Obviously Alkaline, even though Occuring in Chiefly Pyritic Districts.

SECTION VI

FIELD APPLICATION OF CHEMICAL TREATMENT

1. Concept of Field Chemical Treatment

The conclusion to be drawn from Sections IV and V is that sulfide addition to mine drainage waters will eliminate the dissolved metals. However, elimination of ferric iron and aluminum would represent a waste of sulfide, because straightforward neutralization by dilution or addition of relatively inexpensive lime is sufficient to remove these two metals.

Therefore the present investigators conceived the principle of two-stage chemical treatment. In the first stage, neutralization is achieved with lime (solid or slurry) to a certain pH level, and then sulfide is added to remove the remaining objectionable metals.

There would be no objection in principle to adding the two chemicals (lime + sulfide) together, but this would require a foreknowledge of metal concentrations. Control by pH adjustment is simpler and (as shown below) very successful for field adaptation.

The ultimate pH of the treated water was chosen as pH 6.5, because this is the typical ambient pH of waters in the Red Mountain district of southwestern Colorado, where the field study was performed. The pH of treated water in the first stage was chosen as 5.0, since this represents a point where the potential metals of commerce -- Cu and Zn -- are still largely in solution, while Fe and Al are largely precipitated (Fig. 11). The characteristic decline in curves of metal concentration is due to dilution; precipitation is indicated by distinct breaks in the curves. In practice, pH 6.0 might be preferable for transition from Stage 1 to Stage 2, because this represents a greater economy in chemicals cost, but control would be

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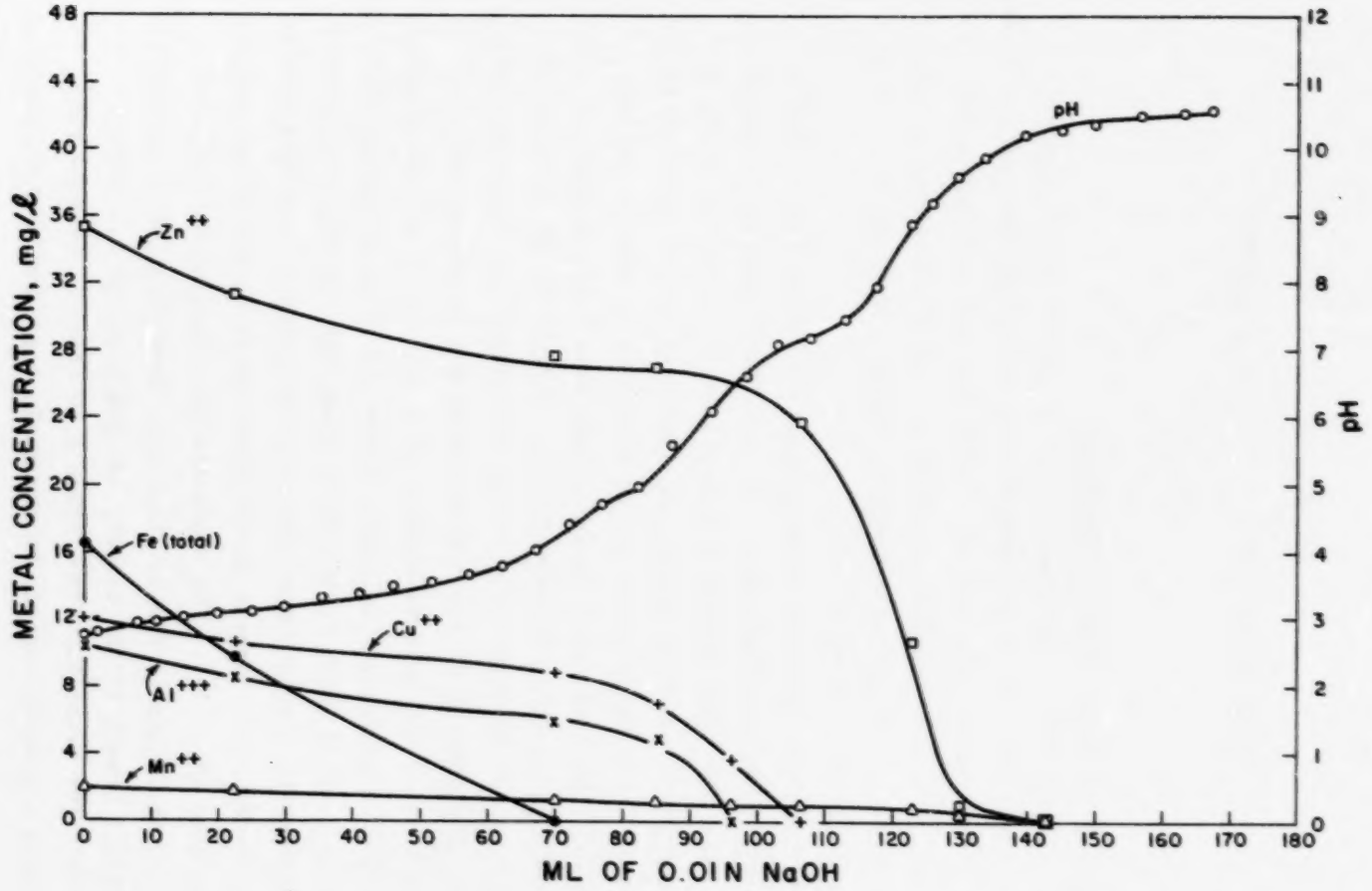

Fig. 11. Neutralization Curves of Water From Mineral Creek (Colorado), Where the Field Study was Performed.

more difficult, particularly in Stage 2. As mentioned above, BaS is the choice for sulfide addition.

The two-stage principle has several features in common with the LHS process developed earlier (5). However, the two-stage process makes use of the steep hydraulic gradients of the Rocky Mountains for mixing, instead of mechanical mixing, and does not require handling of H_2S, or an elaborate mixing system. It is noteworthy that the LHS process does not always remove manganese, the last metal to precipitate in the sulfide series, whereas Mn is definitely removed in the two-stage process described here.

2. Field Experiment: Design

The field installation was constructed on Mineral Creek, at Red Mountain, Colorado. The drawing in Fig. 12 shows the principal features. The pond is 40x20 ft and 3 ft deep, with an adjustable outlet spillway (left). The two treatment stages are achieved in a rectangular wooden vessel (right foreground), which overflows into the distribution trough which feeds the pond. The sulfide chemical supply system is shown to the right of the treatment vessel. The schematic drawing of Fig. 13 shows the key treatment features.

The pond was intended for settling of metal precipitates. It was designed to provide a mean settling time of at least 4 hours, adjustable by means of removable slats in the spillway. The 4-hour settling time was selected so that an 8-hour day would provide twice this much time (i.e., twice the mean), based on the flow rate of Mineral Creek, which was 30 gpm at the time of the experiment.

Mineral Creek was chosen for the field experiment because of its accessibility and its high content of the metals of interest. This creek rises above Red Mountain Pass, and receives drainage from several inactive mines as well as ambient runoff, including rain and snowmelt.

The two treatment stages were designed to contain the stream flow just long enough for mixing with chemicals. Lime is fed either

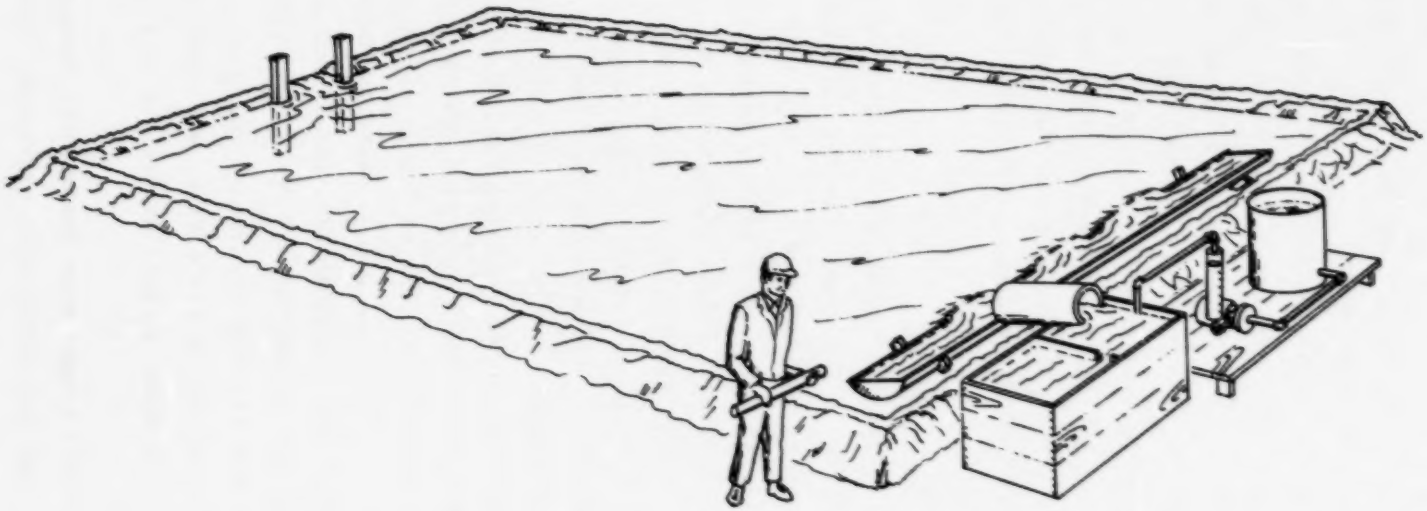

Fig. 12 Illustration of the field installation for treating Mineral Creek by the two-stage process. Water enters the first stage of the rectangular vessel (right foreground). Lime is also fed to the first stage, and sulfide solution is pumped into the second stage.

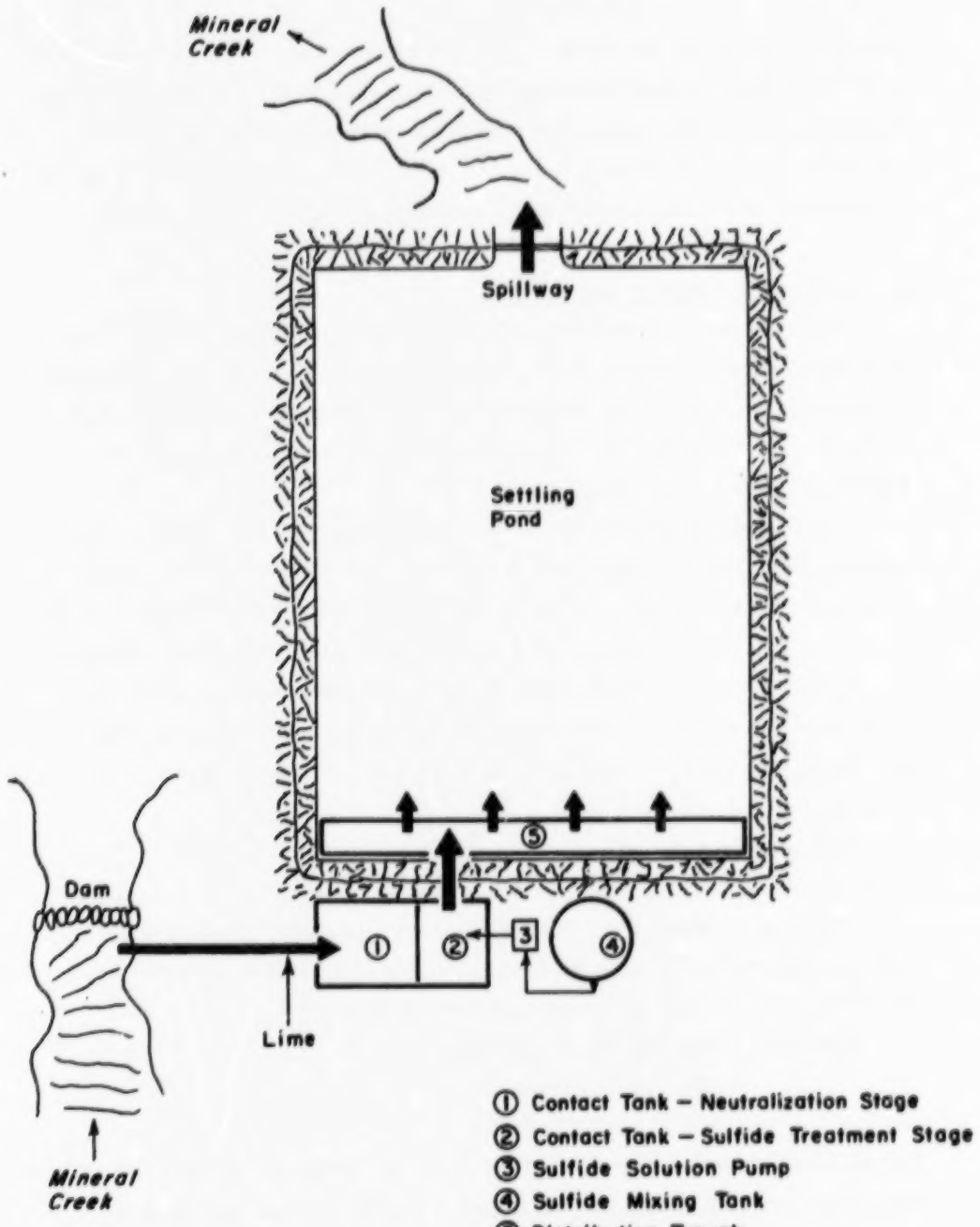

Fig. 13. Schematic Diagram of the Field Installation for Two-stage Treatment.

to the influent or directly into the first stage. Sulfide solution is fed by pump through a rotameter (Fig. 12) into the second stage. Thus the mechanical equipment includes a lime feeder, a sulfide solution pump, and a mixer for the sulfide solution tank. A method of sulfide chemical supply to the tank must also be provided.

3. Field Experiment: Operation

Mineral Creek was diverted as indicated in Fig. 13, and the pond was filled. The pond is shown in Fig. 14, with the equipment in position. (Mr. H. P. Larsen is shown operating the treatment system). A close-up view of the operational facilities at the experimental site is shown in Fig. 15.

Lime feeding proved to be very difficult in the field. Solids feeders could not be employed when even the slightest wind was blowing. This indicates a requirement for delivery of lime slurry by a suitable slurry pump, but then a lime slurry mixing installation is required. In the field experiment, lime was fed manually and sulfide solution was prepared manually, but a centrifugal pump delivered the sulfide solution to Stage 2. Electric power was supplied by a portable generator.

The pH was very simple to control manually. The investigators found that barium sulfide, in the form of "black ash," presented difficulties because it contained only 61 percent BaS by weight*. The balance of black ash is inert, mostly insoluble, and conducive to formation of a friable mass in the mixing tank.

Operating pH conditions were as follows:

pH 5.0 in Stage 1.

pH 6.5 in Stage 2.

Raw Mineral Creek water showed pH 2.6. A cationic surfactant polymer was added at intervals to the Stage 2 effluent, at the rate of

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* Measured in the laboratories of the University of Denver.

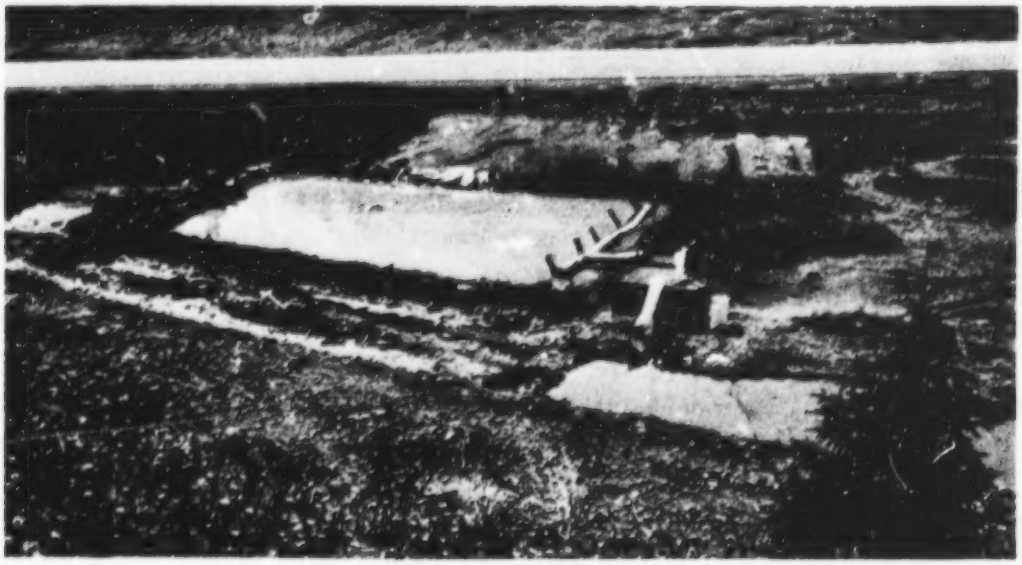

Fig. 14. The Field Installation as Erected, but before the Lime and Sulfide Feeding Apparatus was Added.

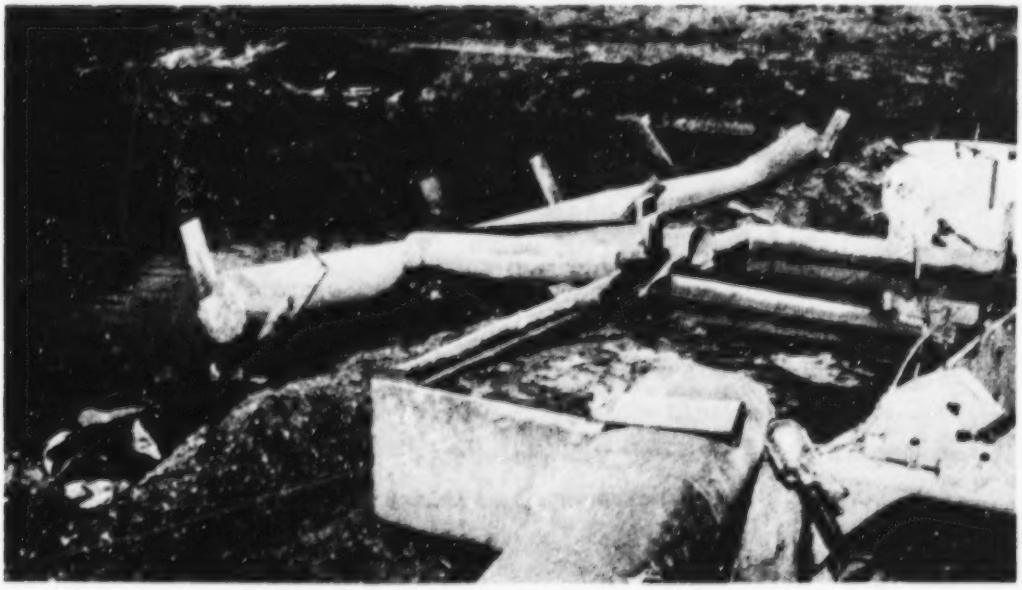

Fig. 15. Close-up of the Treatment Facilities of the Field Installation. In the Foreground is the Two-stage Treatment Vessel.

approximately 0.3 lb surfactant per 1,000 gal creek water.

4. Field Experiment: Results and Observations

The field experiment showed immediately that control of the process by pH control was feasible and simple. The small volume of the treatment stages (35 cu ft in Stage 1, 15 cu ft in Stage 2) contributes to the observed ease of pH control, but the rapid mixing is the most important element in control. This finding is encouraging to the prospects of automatic control of the process.

However, another observation was even more influential to the conduct of the experiment. Although the pond had been carefully designed for hydraulic studies, this proved completely unnecessary, because the sulfide precipitates settled immediately, even collecting in the trough as a characteristic yellow-black slime. By contrast, the yellow ferric hydroxide solids did not precipitate at all, but instead were completely dispersed in the pond water. This phenomenon was as striking and unmistakable as it was unexpected.

The differential settling effect depends strongly on the wind. Overnight, in absence of wind, ferric hydroxide settled out and the pond was clear in the morning.

The sulfide solids accumulated on the bottom of the pond near the distribution trough. The investigators were unable to obtain good photographs of this phenomenon. Nevertheless the accumulation of sulfide solids after only a few hours of operation was very noticeable, and is regarded as very promising for eventual recovery of copper and zinc sulfides, in particular.

During the field experiment, pH was varied in the two stages of treatment in order to provide checks on the effect of different combinations. The results are summarized in the following table:

	Measured pH		Final Concentrations (ppm)					
	Stage 1	Stage 2	Fe (total)	Zn	Mn	Cu	Al	Ni
1.	5.0	5.9	0	12.7	6.4	0	0	≤0.13
2.	5.5	6.4	0	0.3	0.5	0	0	0.13
3.	5.0	5.5	0	30.0	6.8	≤0.5	0	0.29
4.	5.0	5.6	0	30.0	7.1	≤0.3	0	0.19
5.	5.0	6.5	0	0.2	0.4	0	0	0.13

Chromium was also measured, but none was found. Experiment #5 is the standard design condition, which was held at steady state for an extended period.

For the conditions of experiment #5, the following concentrations of the especially toxic metals Hg, Cd and As were found:

Hg	0	ppm
Cd	0.008	ppm
As	0	ppm

5. Laboratory Support for Field Experiment

The project was greatly aided by the availability of the Atomic Absorption Spectrometer of the Department of Metallurgy and Materials Science. Routine analysis of major metal constituents (Fe, Zn, Cu, Mn, Al) was thus made possible.

The Department of Health, State of Colorado, contributed analytical assistance to the project at several times. Their assistance was especially valuable for analysis of heavy metals in very low concentration, where the atomic absorption instrument of the University was not feasible.

In the field experiment, the pH meter of the laboratory of the Department of Chemical Engineering, University of Denver, was used. A portable meter for measurement of pH and oxidation-reduction

potential was loaned by the Field Investigations Branch of the Environmental Protection Agency, Denver, Colorado.

SECTION VII

COMPUTER SIMULATION OF EXPERIMENTAL RESULTS

The laboratory results illustrated in Figs. 3, 4 and 5 suggest that precipitation of dissolved metals can be achieved stoichiometrically in response to sulfide treatment. The field results (Section VI) also show that response to chemical treatment is rapid and sensitive.

For this reason, it is expected that actual mine waters may closely obey the equilibrium relations of Section IV. Equation 12 has accordingly been written for the following cations: Fe^{3+}, Al^{3+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}. Anions included for consideration are OH^- and S^{2-}. Thus there are ten possible equations based on (2), and one each based on eqns. (6), (7) and (8), a total of thirteen equations. Likewise there are thirteen solubility-product and equilibrium constants to be selected.

Butler (8) has pointed out that the very small magnitudes of the quantities in such equations are outside the range of realistic measurement. Thus it is sufficient to find a consistent set of values. Particularly in the case of the sulfide equilibria, eqns. (4) and (5), reported equilibrium constants may vary over two orders of magnitude. Therefore the computer simulation necessarily includes a search for the best choice of a set of K_{sp} and K_e values.

The simulation is needed to predict the behavior of dissolved metals under various combinations of (a) neutralization and (b) sulfide treatment. There will be six algebraic equations to be solved simultaneously in neutralization, and eight in sulfide treatment. Both sets are nonlinear.

For solution, the second-order Newton-Raphson method of iteration (9) was initially chosen to solve the set. The 6x6 and 8x8 matrices

to be solved were approached by means of a standard computer routine available for the Burroughs B 5500 digital computer. The method consisted (in brief) of postulating a volume of solution, beginning with 1 liter of raw mine water of known composition. A volume change was specified, and the system was solved iteratively for the new pH value and new metal concentrations. However, the method failed at about pH 5.6, when the matrix set attained maximum size and the system became extremely sensitive to correct guesses of new concentration values for iteration.

The method ultimately used for the solution of this set of equations was the regula falsi (false position) method, in which the mathematics were less complex than in the Newton-Raphson method. Now the pH is the variable of choice, and the system of equations for iterative solution is illustrated by the following set:

$$x_1 = V_1 \cdot 10^{-pH+0.1} - V \cdot 10^{-pH}$$

$$x_2 = Fe^{+3} - \frac{V \cdot K_{sp,Fe(OH)_3}}{10^{3(pH-14)}}$$

$$x_3 = Al^{+3} - \frac{V \cdot K_{sp,Al(OH)_3}}{10^{3(pH-14)}}$$

$$x_4 = Cu^{+2} - \frac{V \cdot K_{sp,Cu(OH)_2}}{10^{2(pH-14)}}$$

$$x_5 = Zn^{+2} - \frac{V \cdot K_{sp,Zn(OH)_2}}{10^{2(pH-14)}}$$

$$x_6 = Mn^{+2} - \frac{V \cdot K_{sp,Mn(OH)_2}}{10^{2(pH-14)}}$$

where V_1 = previous volume corresponding to pH-0.1
V = new volume, adjustable.
(Metal concentrations are from previous pH conditions.)

A mass balance on the hydroxide ion concentration is written:

$$V \cdot 10^{(pH-14)} = V_1 \cdot 10^{(pH-14.1)} - x_1 - 3x_2 - 3x_3 - 2x_4 - 2x_5 - 2x_6 + (V-V_1)10^{-2}$$

This equation then becomes a function of the volume.

$$F(V) = V_1 \cdot 10^{(pH-14.1)} - V \cdot 10^{(pH-14)} - x_1 - 3x_2 - 3x_3 - 2x_4 - 2x_5 - 2x_6 + (V-V_1)10^{-2}$$

The above sets of equations are iterated until a "V_1" value is reached which approximates the exact solution of $F(V) = 0$.

This set of equations is also nonlinear, but is not as sensitive as the set required by the Newton-Raphson formulation. For solution, pH is incremented by 0.1 in each step. Volume is then incremented, and the respective metal conversions (x_i) found by iterative solution.

In the computation, neutralization by addition of a weak alkaline solution (assumed 0.01 N in OH^-) is applied until a certain pH value is achieved. After this, addition of sulfide solution (also 0.01 N) of the same strength is applied until about pH 11.5, thus achieving two-stage treatment as described in the preceding section.

The computer program, written in ALGOL for implementation on the Burroughs B 5500 digital computer of the University of Denver, is reproduced in Appendix I.

Typical results for neutralization alone are shown in Fig. 16. Water from Mineral Creek, at the location where the field test was conducted, was neutralized, and metal concentrations were monitored (dashed curves). Computed results are given by the solid curves, and the agreement is evidently fairly good. However, it appears that at least one unreported metal species is present, as evidenced

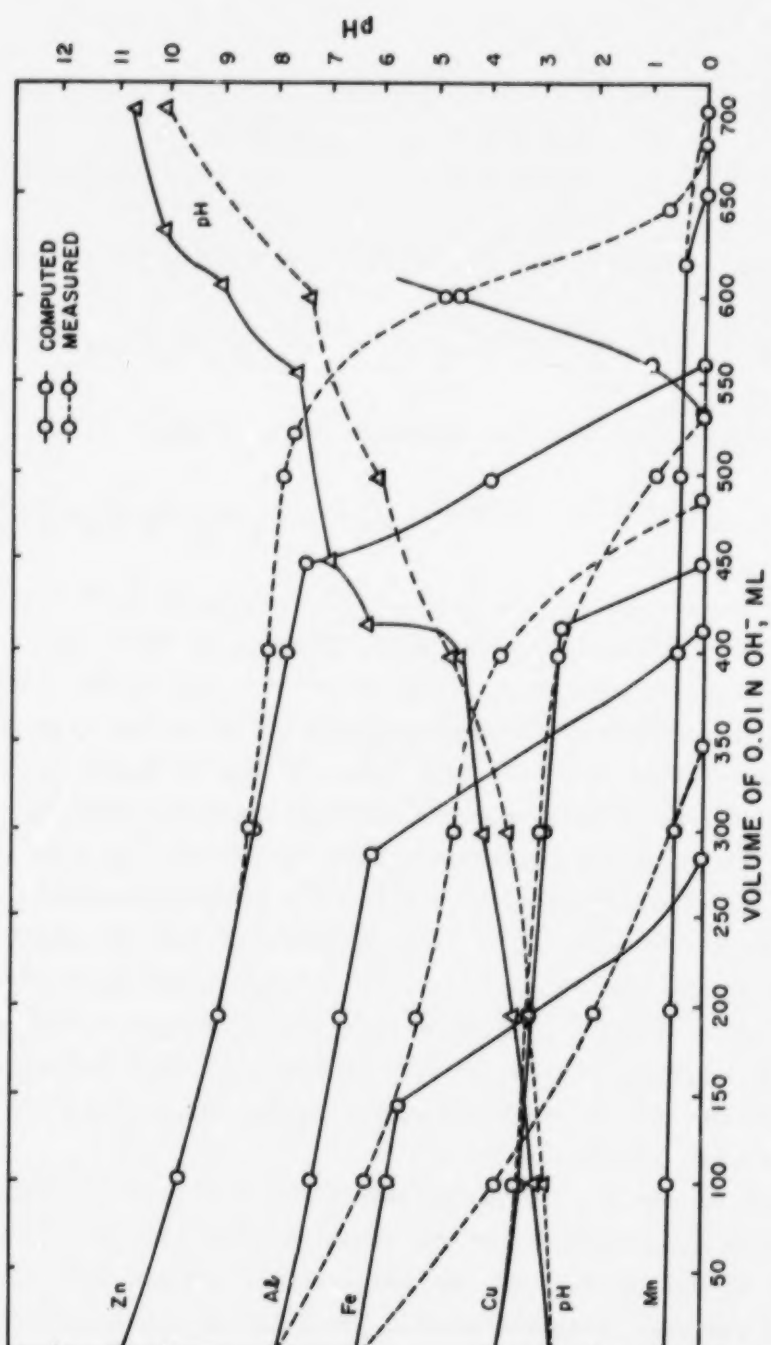

Fig. 16. Comparison of measured and computed neutralization curves for water of Mineral Creek, taken from the pond of Mine K.

by the lag in pH rise (beginning at about 400 ml OH^- addition) and the delay in Zn precipitation, to the extent of about 1 meq. This could possibly be attributed to arsenic, which has been found in concentrations up to 20 mg/l in the nearby pond of Mine K, or to molybdenum, which is common in the Rocky Mountains but which has never been included in measurement series for the Red Mountain region, either by state or federal investigators.

Figures 17, 18, and 19 show computed curves for two-stage treatment based on sulfide addition beginning at pH 4, 5, and 6, respectively.

An important feature of these results is the effect of simple dilution. This imparts the typical negative slope to curves of metal concentration vs. additive chemical volume, before the sharp break point characteristic of a given metal species. If dilution is neglected, which is permissible if solid chemicals are added, the computer simulation is much simplified; typical results are shown in Figs. 20 and 21, compared with experimental results.

Simulated results are considered satisfactory in the case of neutralization alone (Figs. 16, 20), but the case of sulfide addition is more difficult (Fig. 21). The problem resides in the values of K_{sp} available (see above), and possibly also in departures from equilibrium. Many differing values for solubility-product constants are available, but the present investigation chose the following values because they were most consistent with observed results:

Metal	Hydroxide	Sulfide
Ferric iron	1.1×10^{-36}	2.0×10^{-88}
Aluminum	1.2×10^{-32}	--
Cupric copper	6.0×10^{-20}	7.7×10^{-36}
Zinc	7.1×10^{-18}	1.6×10^{-24}
Manganese	1.6×10^{-13}	2.5×10^{-13}

These values were selected from values reported by published

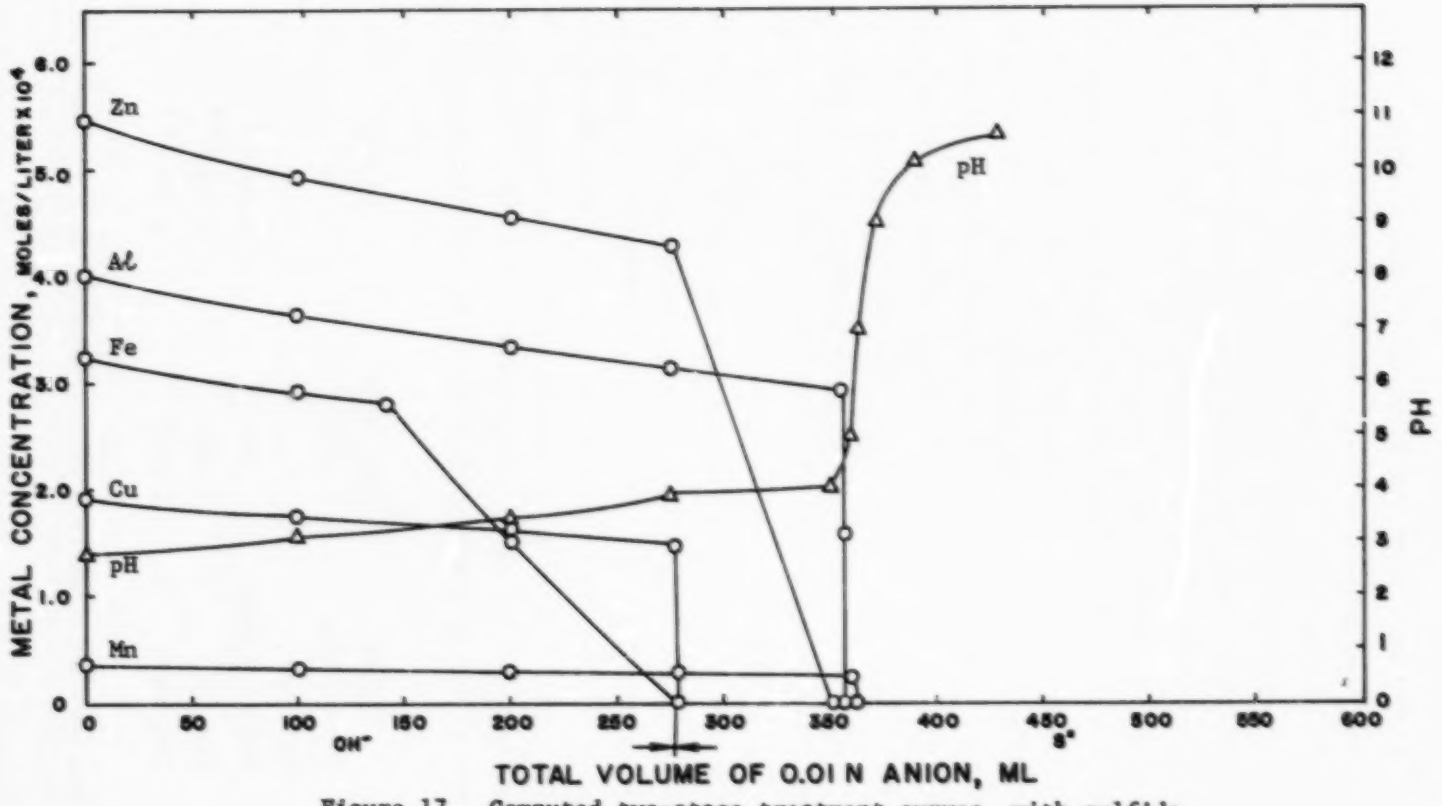

Figure 17. Computed two-stage treatment curves, with sulfide treatment (Stage 2) commencing at pH 4.0.

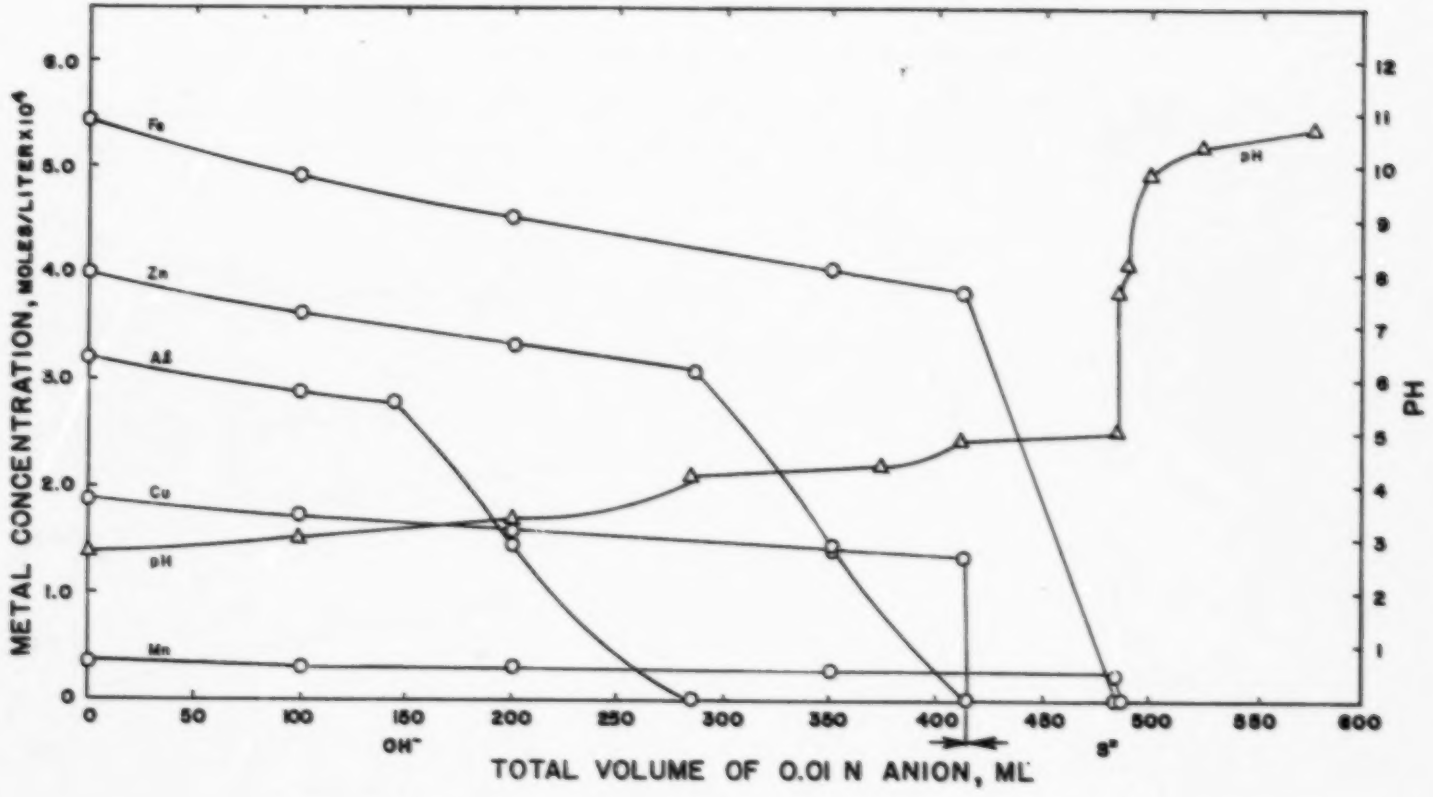

Fig. 18. Computed two-stage treatment curves, with Sulfide Addition (Stage 2) Commencing at pH 5.0.

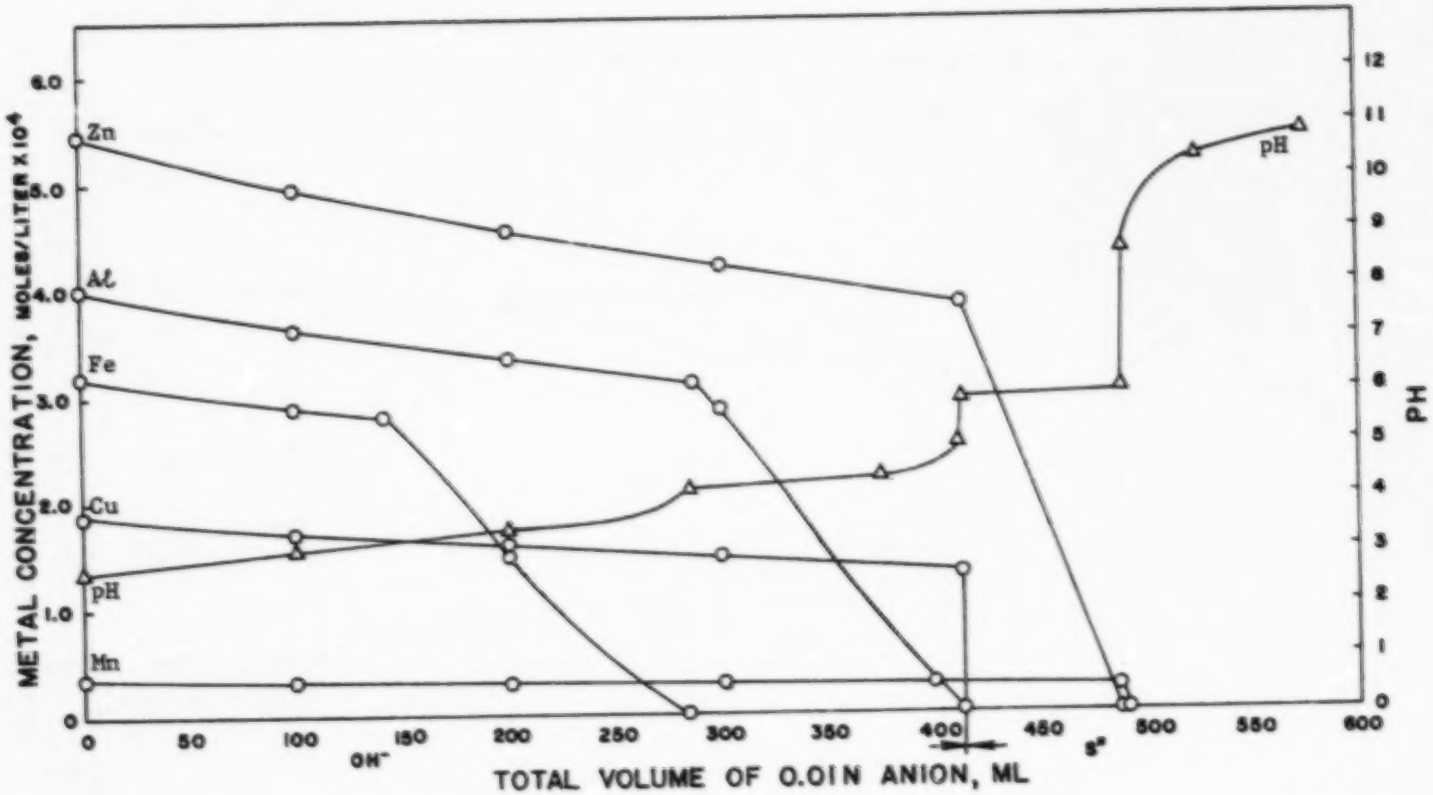

Figure 19. Computed two-stage treatment curves, with sulfide addition (Stage 2) commencing at pH 6.0.

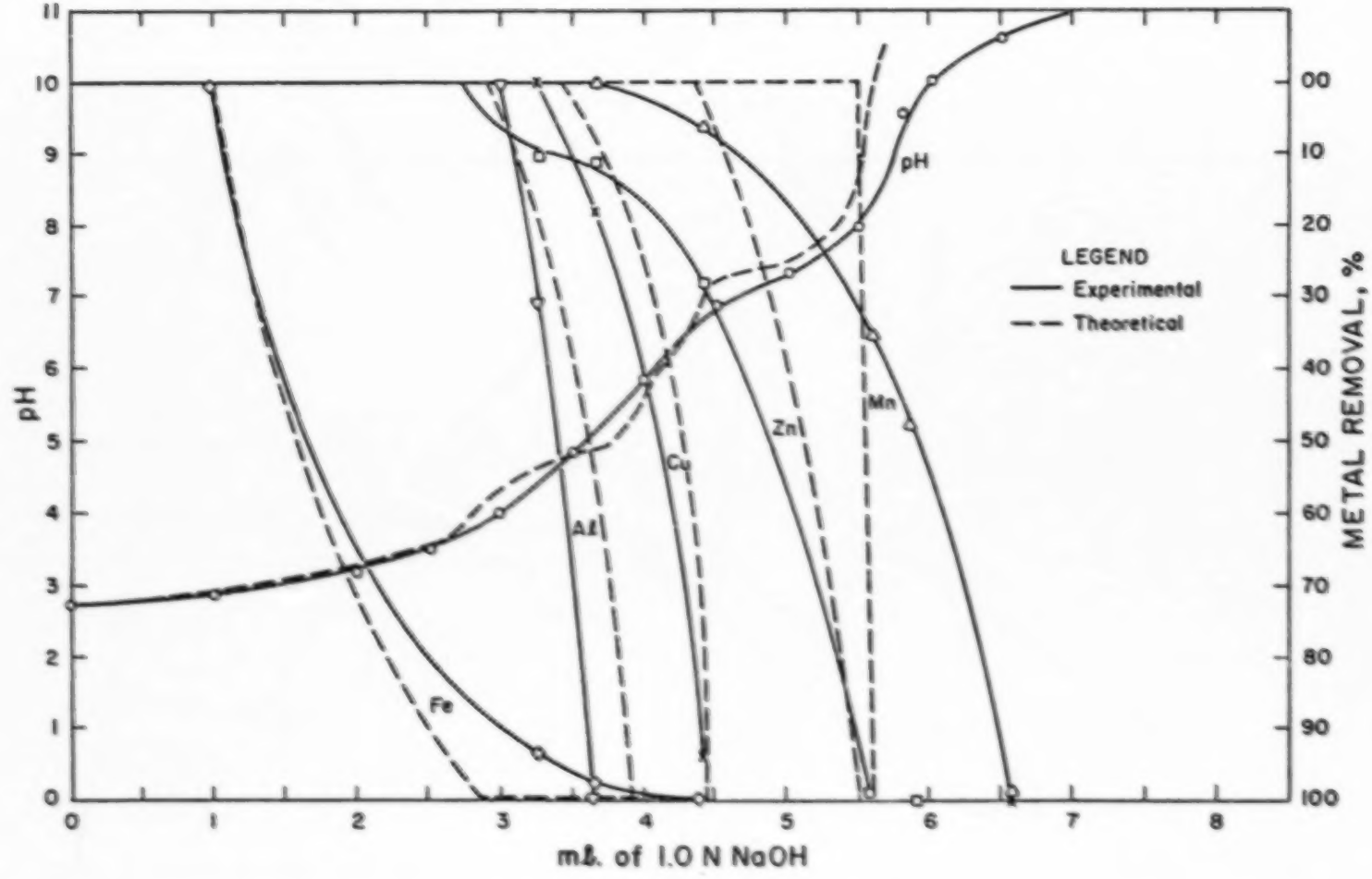

Fig. 20. Comparison of Theoretical and Measured Neutralization Curves, Under the Assumption of no Volume Increase.

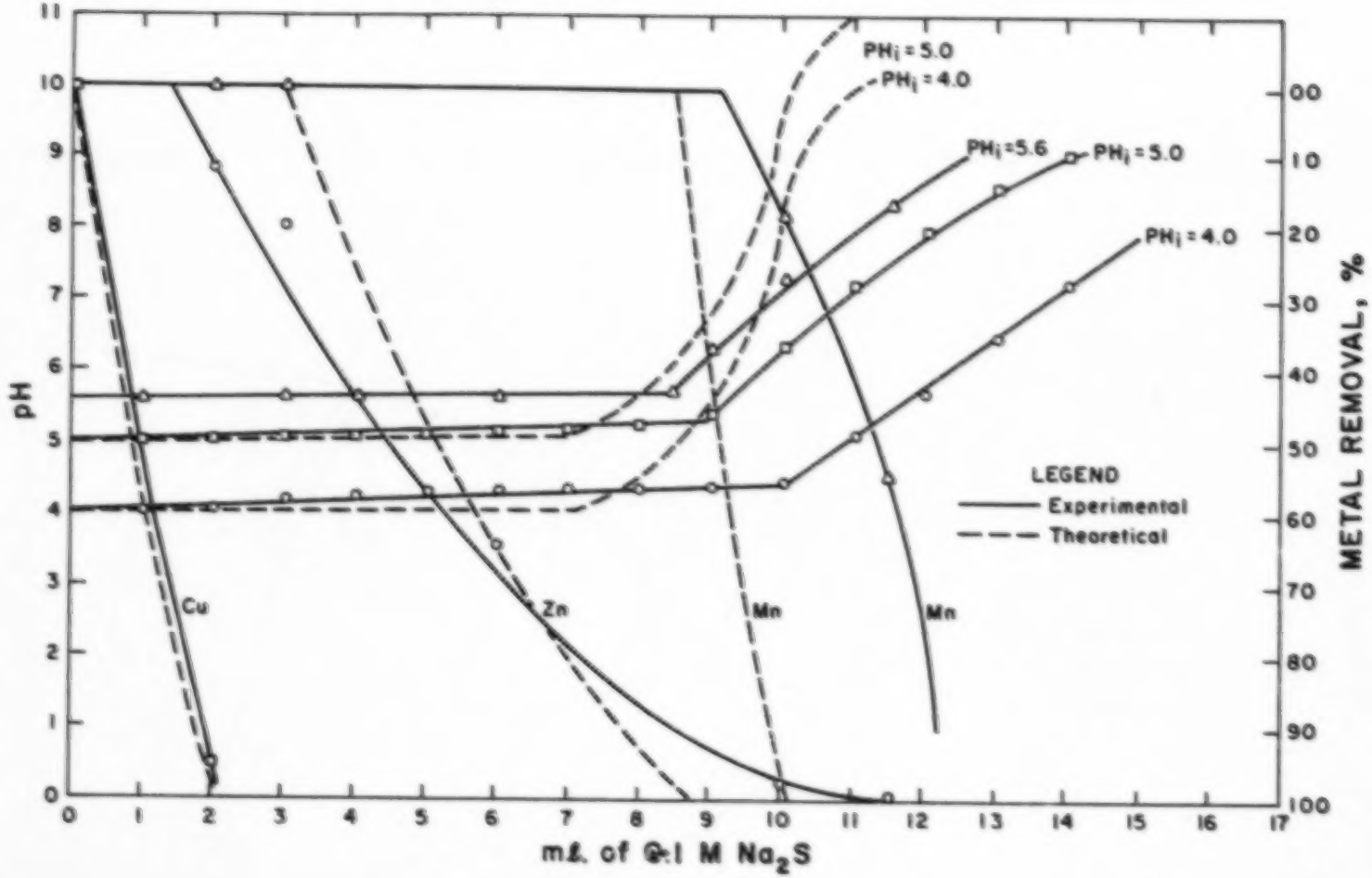

Fig. 21. Comparison of Theoretical and Measured Sulfide Treatment Curves, Under the Assumption of no Volume Increase. pH_i Denotes the Initial pH.

compilations (7,8,10,11). The values for the sulfide equilibrium constants according to eqns. (4) and (5) were selected as follows (8):

$$K_{e_{HS^-}} = 1.3 \times 10^{-13}$$

$$K_{e_{H_2S}} = 1.0 \times 10^{-7}$$

Among previous investigators, only Lanford (12) has reported a process for removal of several metal species in a two-stage treatment process, with supporting equilibrium predictions. Lanford's results cannot be compared with those reported here, for several reason, but principally because Lanford uses a set of K_{sp} values that is quite different from the values adopted here.

SECTION VIII

PRACTICAL ASPECTS OF PRECIPITATION OF HEAVY METALS FROM MINE DRAINAGE WATERS

Facilities Required

The results of the field investigation (Section VI) show that the facilities necessary for chemical treatment are fundamentally simple. The basic requirements include only

(1) complete mixing of chemicals with the drainage water,

(2) sufficient time for settling of precipitates.

For the first requirement, a mixing vessel is necessary, or perhaps two vessels (neutralization + sulfide treatment). For a permanent installation, this mixing capability should consist of a permanent installation, this mixing capability should consist of a basin (concrete, asphalted, wood reinforced, etc.) allowing a few minutes of residence time. No mixing impellers are needed if the hydraulic inflow rate is adequate to give the influent (polluted) stream a vigorous swirling motion that will suspend the added lime. Also required are the following equipment items:

Lime storage hopper
Lime feeder mechanism
Sulfide solution storage vessel
Sulfide solution pump and piping
Sulfide solution mecering gauge
pH controller (optional -- see below).

For the second requirement, an earthen basin is satisfactory. Ferric hydroxide (and probably aluminum hydroxide also) will not settle in this basin unless it is absolutely quiescent, a difficult

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condition to achieve, but possibly attainable by laying a plastic sheet(e.g., polyethylene) over the water surface. However, sulfide compounds will settle in such a basin, and thus an open basin offers a possible method of fractionating sulfides from hydroxides. Residence time in such a pond should be about two hours.

Control

The present investigation has verified that pH is a suitable variable for control of the precipitation process. The pH responds instantaneously to chemical treatment; is a reliable index of relative metal removal; and is easily measurable.

A pH controller, regulating the flow of sulfide solution to the mixing vessel, is perfectly feasible. This would certainly be recommended for large flows and other sensitive pollution situations where the pollution hazard justifies the expense.

Logically, pH would be measured at the outlet of the sulfide treatment stage. (The large time constant of the settling pond indicates that the pond effluent stream is not the proper measurement point for feedback control). This measurement regulates sulfide addition; in principle, the pH of the lime treatment stage (first stage) should also be regulated. However, the lime addition rate is a less important factor in removal of toxic metals, and its adjustment can be achieved manually at given intervals, especially in view of the fact that the concentrations and the flow of most drainage streams do not change significantly within a week or two.

For small operations, manual control may be adequate. The operator would then simply vary the chemical addition rates to chieve the desired pH, on (e.g.) a daily basis.

Economics of Chemical Treatment

It is unlikely that recovered sulfide precipitates can ever pay the complete cost of treating mine drainage waters. However, these sulfides can certainly provide a significant credit against treatment

cost.

Zinc is the principal metal of economic interest, because it is the major toxic metal constituent of mine drainage waters of the Rocky Mountains (Table I). Copper is attractive economically, but it is often present in quantities that yield unsalably low Cu content in the mixed sulfide precipitate. No other metals occur in quantities that suggest recovering them.

In a typical mixed-sulfide precipitate from a treated mine drainage, Cu will constitute 10-15% of the weight, and Zn 25-35%. In addition, a certain amount of dirt and other contaminants will reduce these concentrations by perhaps one-third. Thus the precipitates will yield (optimistically) a return* of

$$\text{Cu} -- 4.5 \times 10^{-4}(a)(b) \quad \$/\text{day}$$
$$\text{Zn} -- 2.1 \times 10^{-4}(a)(b) \quad \$/\text{day}$$

where

a = concentration in mg/l

b = stream flow rate in gpm.

For example, if the stream contains 50 mg/l Cu and is flowing at 100 gpm, then the return is

$$(4.5 \times 10^{-4})(50)(100) = \$22.50/\text{day}$$

It should be emphasized that most smelters will not purchase both metals in a mixed precipitate. That is, they will ususally purchase Cu or Zn but not both.

Costs of processing these concentrates include costs of installation and equipment, collection, and transportation. The present investigation has identified the installation and equipment facilities required, and the chemicals requirement. The required BaS for precipitation of mixed sulfides is about 1000 lb per day (at a price of about $160/ton), and the lime requirement is about 150%

*Estimate based on metals price quotation of 1 January 1972; metal values based on typical smelter schedules of the American Smelting and Refining Company (1971).

of this, at a cost of about $20/ton, all based on a flow rate of 100 gpm and concentrations as cited above.

In conclusion, as a means of estimating the potential value of mixed sulfide precipitates, we define the gross minerals credit (GMC) as follows:

$$\left\{\begin{matrix}\text{gross}\\\text{minerals}\\\text{credit}\end{matrix}\right\} = \left\{\begin{matrix}\text{value of}\\\text{mixed}\\\text{sulfides}\end{matrix}\right\} - \left\{\begin{matrix}\text{cost of}\\\text{treatment}\\\text{chemicals}\end{matrix}\right\}$$

or

$$GMC = SV - CC.$$

Based on metals quotations at the end of calendar year 1971, SV and CC can be estimated by the following relations. For SV (in dollars per day):

$$SV = (0.01202)\cdot F\cdot(C_{Cu}\cdot P_{Cu} + C_{Zn}\cdot P_{Zn}).$$

Symbols have the following meanings:

C_{Zn}, C_{Cu} = Concentration of zinc and copper, respectively, mg/l.

F = Flow rate of stream, hundreds of gpm.

P_{Zn}, P_{Cu} = Price of zinc and copper, respectively, on the metals market, as published in Metal Week, dollars/lb.

The chemicals cost (CC) may be estimated from the following relation (CC in dollars per day):

$$CC = \left[C_{Fe^{3+}}/55.84 + C_{Al^{3+}}/27.0 \right] \cdot F\cdot(4.7\times10^{-2})\cdot P_{CaO} + \left[C_{met} \right] \cdot F\cdot(2.4\times10^{-2})\cdot P_{BaS}$$

where $C_{Fe^{3+}}$, $C_{Al^{3+}}$ = Concentration of ferric iron and aluminum, respectively, mg/l.

C_{met} = Concentration of all other metallic species except Fe^{3+} and Al^{3+}, mg/l.

P_{CaO}, P_{BaS} = Unit cost of CaO and BaS, respectively, $/lb.

It should be noted that GMC is exclusive of all operating and transportation costs, as well as capital cost of facilities. The smelter will discount the value of the concentrate for contamination, and will impose certain surcharges. Smelter schedules are available from the smelting companies upon request.

Use of Flocculant Chemicals

The field results (Section VI) indicate that there is probably some advantage to be gained by adding a flocculating agent in two-stage chemical treatment. The pronounced sedimentation behavior observed in the field, where a flocculant was added, was much better than laboratory results (13) led the investigators to expect.

Very little information is available on this subject. A useful paper on flocculation of metallic hydroxides from mine waters has recently been published (14), and the present investigation has included a series of measurements of the rate of sedimentation of mixed sulfides upon addition of various quantities of a cationic surfactant as flocculant (Fig. 22). There is clearly some advantage to be gained by use of surfactant flocculants, but each mine drainage situation must be evaluated separately.

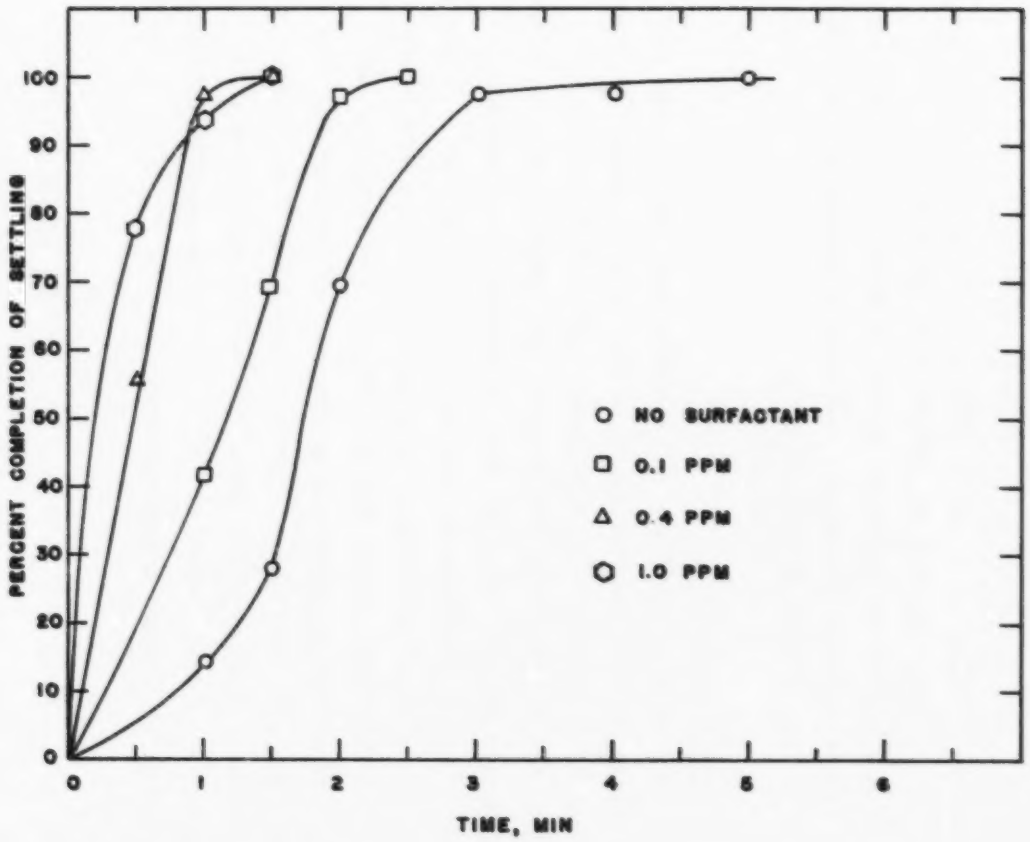

Fig. 22. Settling Tests for a Mixed Metal Sulfide Floc As a Function of Surfactant Addition. Water from Mine BH (Idaho). Surfactant: Calgon M-590. pH 5.5.

SECTION IX

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APPENDIX I

COMPUTER PROGRAM FOR CALCULATION OF EQUILIBRIUM IN TREATED MINE DRAINAGE WATERS

```
        BEGIN
FILE IN         CARD (2, 10);
FILE OUT        LINE 1 (2, 15);
REAL            PH, V, V1, TEMP1, TEMP2, DELV, H2S, STOT, SOLD, FV, HS,
                SBLK, CHANGE, VTEMP, FES, ALS, CUS, ZNS;
INTEGER         I, Z, S1, S2, J, PL;
ARRAY           M,X,KSP,C,MP,MCE[0:8],
                KS[1:8],Y[1:8],PHS, VS,Y1S,Y2S,Y3S[0:150];
LABEL           DONE,TOP,RESULT,SULFUR,ANSWER,HEAD,HALF,MIDDLE,FINIS,
                ANFANG;
FORMAT          F1 (5R10.6);

FORMAT          POT (X6,"FE3",X11,"AL",X12,"CU",X12,"ZN",X12,"MN",X12,
                "PH",X12,"V");

FORMAT          F2 (7(X1,E12.5X1));

FORMAT          F3 ("END OF PROGRAM");

FORMAT          F5 (" INITIAL OH KSP VALUES FE+3 = ",E10.2," AL = ",
                E10.2," CU = ",E10.2," ZN = ",E10.2," MN = ",E10.2);

FORMAT          F6 (1R10.6);

FORMAT          F7 ("CHANGE FROM OH- TO S-- ADDITION");

FORMAT          F8 (4R10.6);
```

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```
FORMAT          F11 (3R10.6);

FORMAT          F12 ( " INITIAL SULFIDE KSP VALUES FE+3 = ",E10.2,
                " CU = ",E10.2," ZN = ",E10.2, " MN = ",E10.2);

FORMAT          F14 (5(X1,E12.5X1));

FORMAT          F21 (X6,"Y1",X12,"Y2",X12,"Y3",X12,"PH",X12,"V");

COMMENT     THE DATA IS READ IN AS THE KSP HYDROXIDE VALUES OF FE3,AL,
            CU,ZN,MN,ON THE FIRST CARD, THEIR CONCENTRATIONS IN MOLES ON
            THE SECOND CARD, THE PH, ORIGINAL VOLUME, AND THE DELTA
            VOLUME ON THE THIRD CARD, THE SULFIDE KSP VALUES ARE THEN
            READ, H2O, HS, H2S ON THE FOURTH CU, ZN, FE+3, AND MN ON
            THE FIFTH, THE CHANGE FROM OH TO S-- PRECIPITATION ON THE
            SIXTH CARD;
                READ (CARD,F1,KSP[2],KSP[3],KSP[4],KSP[5],KSP[6];
                READ (CARD,F1,M[2],M[3],M[4],M[5],M[6]);
                READ (CARD,F11,PH,V1,DELV);
                READ (CARD,F11,KS[1],KS[2],KS[3]);
                READ (CARD,F8,KS[4],KS[6],KS[7],KS[8]);
                READ (CARD,F6,CHANGE);
ANFANG:         WRITE (LINE,F5,KSP[2],KSP[3],KSP[4],KSP[5],KSP[6]);
                WRITE (LINE,F12,KS[7],KS[4],KS[6],KS[8]);
                WRITE (LINE,POT);
                WRITE (LINE,F2,M[2],M[3],M[4],M[5],M[6],PH,V);
                KS[5] ← KSP[3];
                V ← V1 + DELV;
                S1 ← 0; S2 ← 0; PL ← 0;
                Z ← 2;  J ← 1;
                FES ← M[2]; ALS ← M[3]; CUS ← M[4]; ZNS ← M[5];
                FOR I ← 0 STEP 1 UNTIL 1 DO
```

```
        BEGIN
                M[I] ← 0; X[I] ← 0; KSP[I] ← 0; C[I] ← 0; MP[I] ← 0;
                MCE[I] ← 0;
        END;
                C[2] ← 3; C[3] ← 3; C[4] ← 2; C[5] ← 2; C[6] ← 2;
                IF PH ≥ CHANGE THEN GO TO SULFUR;
TOP:            FOR I ← 2 STEP 1 UNTIL 6 DO
        BEGIN
                MCE[I] ← (VxKSP[I]) / (10*(C[I]x(PH-14)));
                X[I] ← M[I] - MCE[I];
                IF X[I] ≤ 0  THEN X[I] ← 0;
                IF PH > 6.7  THEN X[3] ← 0;
        END;
                IF PH > 4.0  THEN IF PH ≤ 8.8  THEN
        BEGIN
                MCE[2] ← (Vx2.5x10*(-17)) / 10*(PH - 14);
                X[2] ← M[2] - MCE[2];
                IF X[2] ≤ 0  THEN X[2] ← 0;
                X[2] ← X[2] / 3;
        END
                ELSE IF M[2] ≤ FES THEN
        BEGIN
                X[2] ← Vx3.2x10*(-5)x10*(PH-14) - M[2];
                X[2] ← X[2] / 3;
        END;
                IF PH > 6.7  THEN IF M[3] ≤ ALS THEN
        BEGIN
                X[3] ← V x 3x10x10*(PH-14) - M[3];
                X[3] ← X[3] / 3;
        END:
                IF PH > 9.5 THEN IF M[4] ≤ CUS THEN
```

```
        BEGIN
                X[4]← V x 7.1x10*(-6)x10*(PH-14) - M[4];
                X[4]← X[4] / 2;
        END
                IF PH > 9.9 THEN IF M[5] ≤ ZNS THEN
        BEGIN
                X[5]← Vx1.2x10*(-3)x10*(PH-14) - M[5];
                X[5]← X[5] / 2;
        END;
COMMENT THE PROGRAM USES A DELTA PH OF 0.1 ;
                X[1]← V1 x 10 * (-PH+0.1) - V x 10 * (-PH);
                FV← V1x10*(PH-14.10) - Vx10*(PH-14) - X[1] - 3xX[2] -
                3xX[3] - 2xX[4] - 2xX[5] - 2xX[6]+(V-V1)x10*(-2);
COMMENT A TEST IS MADE FOR CONVERGENCE;
                IF PL = 5 THEN GO TO RESULT;
                IF S1 = 1 THEN IF S2 = 2 THEN PL← PL + 1;
COMMENT THE NEW VOLUME,V, IS ADJUSTED ;
                IF FV ≤ 0 THEN
        BEGIN
                IF S1 = 1 THEN TEMP2 ← 0.5 x TEMP1 ELSE TEMP2 ← DELV;
                S2 ← 2;
                V ← V + TEMP2;
        END
                ELSE
        BEGIN
                IF S2 = 2 THEN TEMP1← 0.5 x TEMP2 ELSE TEMP1 ← 0.5 x
                DELV;
                S1 ← 1;
                V ← V - TEMP1;
        END;
                GO TO TOP;
RESULT:         IF PH > 4.0 THEN X[2] ← 3xX[2];
```

```
                IF PH > 6.7 THEN X[3] ← -3xX[3];
                IF PH > 8.8 THEN X[2] ← -X[2];
                IF PH > 9.5 THEN X[4] ← -2xX[4];
                IF PH > 9.9 THEN X[5] ← -2xX[5];
                FOR I ← 2 STEP 1 UNTIL 6 DO
                M[I] ← M[I] - X[I];
                FOR I ← 2 STEP 1 UNTIL 6 DO
                MP[I] ← M[I]/V;
COMMENT  THE RESULTS ARE PRINTED OUT WITH THE METAL CONCENTRATIONS IN
        MOLES PER LITER;
                WRITE (LINE, F2,MP[2],MP[3],MP[4],MP[5],MP[6],PH,V);
                FOR I ← 2 STEP 1 UNTIL 6 DO
        BEGIN
                IF M[I] ≤ 0 THEN
                M[I] ← 0;
        END;
                PHS[J] ← PH; VS[J] ← V; Y1S[J] ← X[1]; Y2S[J] ← 0;
                Y3S[J] ← 0;  J ← J + 1;
                S1 ← 0; S2 ← 0; PL ← 0;
                V1 ← V;
                V ← V + DELV;
                PH ← PH + 0.1;
                IF PH ≥ CHANGE THEN GO TO SULFUR;
                GO TO TOP;
SULFUR:         S1 ← 0; S2 ← 0; SOLD ← 0; H2S ← 0; HS ← 0;
                DELV ← DELV / 2;
                WRITE (line,F7);
                M[7] ← M[2]; M[8] ← M[6]; M[6] ← M[5]; M[5] ← M[3];
                FOR I ← 1 STEP 1 UNTIL 8 DO
                Y[I] ← 0;
HEAD:           Y[1] ← V1x10*(PH-14.1) - Vx10*(PH-14);
                Y[2] ← (10*(-PH)x(SOLD + (V-V1)x10*(-2) + (K3[2]xHS)/
                (10*(-PH)+K3[3])) - K3[2]x(HS+(K3[3]xH2S)/(10*(-PH) +
```

```
                KS[3])))/(10*(-PH)+KS[2]-(KS[2]x10*(-PH))/(10*(-PH) +
                KS[3]));
                Y[3] ← ((10*(-PH))x(HS+Y[2])-KS[3]xH2S)/(10*(-PH)+KS[3]);
                FV ← -Vx10*(-PH) + V1 x 10*(-PH+0.1)-Y[1]-Y[2]-Y[3];
                STOT ← SOLD - Y[2] + 10*(-2)x(V-V1);
COMMENT  A TEST IS MADE FOR CONVERGENCE;
                IF PL = 7 THEN GO TO HALF;
                IF S1 = 1 THEN IF S2 = 2 THEN PL ← PL + 1;
                IF FV ≥ 0 THEN
        BEGIN
                IF S1 = 1 THEN TEMP2 ← 0.5 x TEMP1 ELSE TEMP2 ← DELV;
                S2 ← 2;
                V ← V + TEMP2;
        END
                ELSE
        BEGIN
                IF S2 = 2 THEN TEMP1 ← 0.5 x TEMP2 ELSE TEMP1 ← 0.5 x
                DELV;
                S1 ← 1;
                V ← V - TEMP1;
        END;
                GO TO HEAD;
HALF:           SOLD ← SOLD - Y[2] + 10*(-2)x(V-V1);
                STOT ← SOLD; S1 ← 0;  S2 ← 0;
                IF STOT ≤ 0 THEN GO TO ANSWER;
                V1 ← V;  V ← V + DELV;  PL ← 0;
COMMENT  A SULFIDE CONCENTRATION WHICH SATISFIES THE PH CONDITION IS
        CALCULATED FIRST.  THEN THE CORRESPONDING PRECIPITATIONS FOR
        THAT SULFIDE CONCENTRATION ARE CALCULATED;
MIDDLE:         MCE[4] ← ((V*2)xKS[4])/STOT;
                SBLK ← STOT x 10*10;
COMMENT  KS[7] IS FROM LINKE AND EQUALS 1.45 x 10-87;
                MCE[7] ← ((V*5)xKS[7])x(SOLK*(-3));
```

```
                MCE[7] ← MCE[7] x 10*(-14);
                IF MCE[7] ≤ 0 THEN MCE[7] ← 0 ELSE MCE[7]← SQRT(MCE[7]);
                MCE[6] ← ((V*2)xKS[6])/STOT;
                MCE[8] ← ((V*2) x KS[8])/STOT;
                MCE[5] ← (VxKS[5]) / (10*(C[3]x(PH-14)));
                FOR I ← 4 STEP 1 UNTIL 8 DO
        BEGIN
                Y[I] ← M[I] - MCE[I];
                IF Y[I] ≤ 0 THEN Y[I] ←0;
        END;
                Y[7] ← 0.5 x Y[7];
                FV ← -Y[4]-Y[6]-3xY[7]-Y[8]+(V-V1)x10*(-2);
COMMENT  A TEST IS MADE FOR CONVERGENCE;
                IF PL = 5 THEN GO TO ANSWER;
                IF S1 = 1 THEN IF S2 = 2 THEN PL ← PL + 1;
COMMENT  THE NEW VOLUME,V, IS ADJUSTED SO THAT FV IS MINIMUM;
                IF FV ≤ 0 THEN
        BEGIN
                IF S1 = 1 THEN TEMP2 ← 0.5 x TEMP1 ELSE TEMP2 ← DELV;
                S2 ← 2;
                V← V + TEMP2;
        END
                ELSE
        BEGIN
                IF S2 = 2 THEN TEMP1← 0.5 x TEMP2 ELSE TEMP1 ← 0.5 x
                DELV;
                S1 ← 1;
                V ← V - TEMP1;
        END;
                GO TO MIDDLE;
ANSWER:         FOR I ← 4 STEP 1 UNTIL 8 DO
        BEGIN
                M[I] ← M[I] - Y[I];
                IF M[I] ≤ 0 THEN M[I] ←0;
```

```
                MP[I] ← M[I]/V;
        END;
                WRITE (LINE,F2,MP[7],MP[5],MP[4],MP[6],MP[8],PH,V);
                PHS[J] ← PH; VS[J] ← V; Y1S[J] ← Y[1]; Y2S[J] ← Y[2];
                Y3S[J] ← Y[3]; J ← J + 1;
                S1 ← 0; S2 ← 0;
                V1 ← V;
                V ← V + DELV;
                PL ← 0;
                HS ← HS + Y[2] -Y[3];
                IF HS ≤ 0 THEN HS ← 0;
                H2S ← H2S + Y[3];
                IF H2S ≤ 0 THEN H2S ← 0;
                PH ← PH + 0.1;
                IF PH ≥ 11.6 THEN GO TO DONE;
                GO TO HEAD;
DONE:           WRITE (LINE[PAGE]);
                WRITE (LINE,F21);
                WRITE (LINE,F14,FOR I ← 1 STEP 1 UNTIL J DO[Y1S[I],
                Y2S[I],Y3S[I],PHS[I],VS[I]]);
                CHANGE   5.0;
FINIS:          WRITE (LINE,F3);
        END.
```